13.64; MS, m/e 140 (82), 125 (100). The E isomer eluted second in 59.2% yield and showed the following: IR (neat) 1740 and 1670 cm^{-1}; ^1H NMR δ 6.66 (tt, 1 H, J = 7.3, 2.9 Hz), 4.30 (t, 2 H, J = 7.4 Hz), 2.79 (m, 2 H), 2.15 (m, 2 H), 1.40 (sextet, 2 H, J = 7.0 Hz), 0.88 (t, 3 H, J = 7.2 Hz); ^{13}C NMR δ 171.10, 140.42, 125.20, 65.22, 31.96, 24.84, 21.22, 13.58; MS, m/e 140 (33), 99 (100).

α-Cyclohexylidene-γ-butyrolactone. This material was prepared in 60% yield and showed the following properties: IR (neat) 1740 and 1655 cm^{-1}; ^1H NMR δ 4.22 (t, 2 H, J = 7.3 Hz), 2.82 (bt, 2 H, J = 7.1 Hz), 2.15 (m, 2 H), 1.56 (m, 6 H), 1.19 (m 1 H), 0.82 (m, 1 H); ^{13}C NMR δ 170.58, 157.62, 115.09, 64.21, 34.18, 28.32, 27.81, 27.65, 27.13, 25.95; MS, m/e 166 (100).

(*E*)-α-(α-Methylbenzylidene)-γ-butyrolactone. This material was prepared in 50% yield and showed the following properties: IR 1748, 1645 cm^{-1}; ^1H NMR δ 7.45–7.09 (m, 5 H), 4.33 (t, 2 H, J = 7.5 Hz), 3.01 (tq, 2 H, J = 7.5, 1.8 Hz), 2.16 (t, 3 H, J = 1.8 Hz); ^{13}C NMR δ 168.5, 150.2, 139.8, 127.8, 127.7, 127.3, 119.9, 63.8, 28.2, 24.9; MS, m/e 189 (14), 188 (100). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.59; H, 6.38. Found: C, 76.63; H, 6.44.

α-Butylidene of Cis Lactone of 2-Hydroxycyclohexaneacetic Acid. Following the general procedure above, 0.2 g (0.6 mmol) of **3** was deprotonated with 0.7 mmol of LDA, and the resulting enolate anion was quenched with 0.10 mL (0.085 g; 1.18 mmol) of n-butyraldehyde to give, after alumina chromatography, 0.052 g (39.7%) of a 55:45 E:Z mixture of the title compound: IR 1745, 1675 cm^{-1}; ^1H NMR δ 6.59 (dt, J = 7.7, 1.3 Hz, vinyl proton of E isomer), 6.03 (dt, J = 7.7, 1.8 Hz, vinyl proton of Z isomer), 4.58–4.26 (m, $^1/_2$ H), 3.08–2.75 (m, $^1/_2$ H), 2.63 (dt, J = 7.5, 1.3 Hz), 2.22 (t, J = 6.8 Hz), 2.14 (t, J = 7.5 Hz), 1.95–1.08 (m, 10 H), 0.94 (t, 3 H, J = 6.8 Hz); ^{13}C NMR δ 171.5, 170.5, 141.4, 138.0, 134.3, 127.7, 76.4, 40.7, 37.3, 31.4, 29.3, 28.5, 27.3, 27.2, 26.9, 22.7, 22.4, 21.9, 21.4, 20.4, 19.2, 13.7, 13.6, GC–MS Z isomer (retention time 9.44 min) 195 (13), 194 (100); E isomer (retention time 10.26 min) 195 (15), 194 (100).

Reaction of 1 with 4-Cholesten-3-one: Preparation of 5. Following the general procedure above, 1.41 g (5 mmol) of **1** was deprotonated with 5.75 mmol of LDA, and the enolate was quenched with 1.92 g (5 mmol) of 4-cholesten-3-one to give, after crystallization from hexane, 0.67 g (30%) of the title product: IR 1728, 1620 cm^{-1}; ^1H NMR δ 7.39 (s, 1 H), 4.30 (t, 2 H, J = 7.7 Hz), 2.88 (t, 1 H, J = 7.7 Hz), 2.44–2.12 (m, 3 H), 2.12–1.10 (m, 26 H), 1.07 (s, 3 H,), 0.94 (s, 3 H), 0.89 (s, 3 H), 0.69 (s, 3 H); ^1H NMR (benzene-d_6) δ 7.97 (s, 1 H), 3.64 (t, 2 H, J = 7.7 Hz), 2.27 –1.87 (m, 4 H), 1.87–1.12 (m, 26 H), 0.97 (s, 3 H), 0.93 (s, 3 H), 0.90 (s, 3 H), 0.68 (s, 3 H); ^{13}C NMR δ 170.6, 157.5, 148.0, 117.6, 113.2, 64.5, 56.2, 56.1, 54.1, 42.4, 39.8, 39.5, 37.8, 36.2, 35.8, 33.0, 32.6, 28.2, 28.0, 27.6, 26.1, 24.2, 23.8, 22.8, 22.5, 21.2, 18.7, 17.8, 11.9: MS, m/e 454 (33), 453 (100). Anal. Calcd for $C_{31}H_{48}O_2$: C, 82.18; H, 10.59. Found: C, 82.04; H, 10.75.

Reaction of 2 with Dodecanedialdehyde. Preparation of 7 and 8. A standard apparatus of 100-mL capacity was charged with 1.7 mL (12 mmol) of diisopropylamine and 20 mL of THF. This was converted to LDA with 12 mmol of n-butyllithium and 3.2 g (10.8 mmol) of **2** in 10 mL of THF was added dropwise at −78 °C followed by stirring at that temperature for 45 min and then the addition of 0.99 g (5 mmol) of dodecanedialdehyde. The solution was allowed to reach room temperature and was refluxed for 15 min, and 6.38 mL (50 mmol) of trimethylchlorosilane was added to silylate the diphenylmethylsiloxide produced. The reaction mixture was then diluted with hexane (10 mL), washed with water (2 × 15 mL), and dried over magnesium sulfate. After solvent removal at reduce pressure, the product was purified by column chromatography on alumina, eluting with hexane followed by 5% dichloromethane, to yield 1.81 g (98%) of **7** and **8**, which were crystallized from ether/hexane. The E,Z diastereomer (20% of the mixture) eluted first and showed the following: IR (neat) 1755 and 1675 cm^{-1}; ^1H NMR δ 6.72 (tt, 1 H, J = 7.5, 2.9 Hz), 6.17 (tt, 1 H, J = 7.8, 2 Hz), 4.9–4.4 (m, 1 H), 3.2–2.8 (m, 4 H), 2.7–2.4 (m, 4 H), 2.3–1.3 (m, 16 H), 1.4 (d, 3 H), J = 6.4 Hz), 1.38 (d, 3 H, J = 6.4 Hz); ^{13}C NMR δ 170.88, 169.75, 144.01, 140.76, 126.46, 124.73, 73.91, 73.64, 36.86, 32.90, 29.33, 28.08, 27.54, 22.23, 21.74; MS, m/e 110 (100), 182 (45). The E,E diastereomer (80%) eluted second and showed the following: IR (neat) 1755 and 1680 cm^{-1}; ^1H NMR δ 6.72 (tt, 1 H, J = 7.5, 2.9 Hz), 4.9–4.4 (m, 1 H), 3.2–2.8 (m, 2 H), 2.7–2.4 (m, 2 H), 2.3–1.3 (m, 8 H), 1.4 (d, 3 H, J = 6.2 Hz); ^{13}C NMR δ 170.92, 140.79, 126.53, 73.96, 32.94, 30.17, 29.35, 28.13, 22.27; MS, m/e 110 (100), 182 (45). Anal. Calcd for $C_{22}H_{34}O_4$: C, 72.99; H, 9.39. Found: C, 72.70; H, 9.47.

Preparation of (±)-Ancepsenolide (9). A standard apparatus of 50-mL capacity was charged with 0.02 g (0.17 mequiv of Ni) of Raney nickel and 10 mL of benzene. This was refluxed for 3 h to deactivate it somewhat and 0.02 g (0.06 mmol) of **7** added in 5 mL of benzene and this solution refluxed for 20 h. The Raney nickel was washed with hot benzene, and the solution was evaporated to give a solid, which was crytallized from methanol to give 0.16 g (80%) of the title compound. The synthetic material was identical in all respects with the natural material.

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Reaction of α-Silyl Esters with Grignard Reagents: A Synthesis of β-Keto Silanes and Ketones. Preparation of the Douglas Fir Tussock Moth Pheromone[1]

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A variety of α-diphenylmethylsilyl esters have been prepared and reacted with Grignard reagents. The reaction is relatively slow in refluxing THF and can be controlled to allow the addition of 1 equiv of the Grignard reagent, providing the corresponding β-keto silane. Protiodesilylation of the β-keto silane results in the overall conversion of an ester to a ketone. This ester to ketone methodology has been applied to a two-step synthesis of the pheromone of the Douglas fir tussock moth. The β-keto silanes are viable precursors to regioselectively generated enol silyl ethers. The reaction of ethyl 2-methyl-2-(diphenylmethylsilyl)propionate with vinylmagnesium bromide or 2-methyl-1-propenylmagnesium bromide results in the addition of 2 equiv of the Grignard reagent, the second in a Michael fashion.

The preparation of ketones via the reaction of organometallic reagents and carboxylic acid derivatives represents a logical, but not always trouble-free, transformation.[5] Although enolization and reduction of the ketone resulting

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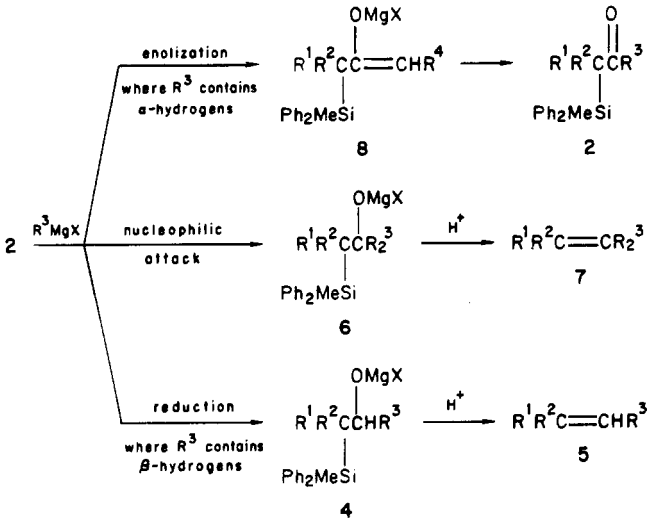
Table I. Ethyl α-Diphenylmethylsilyl Esters

entry	ester	R^1	R^2	% yield (isolated)
1	**1a**	CH_3	H	83
2	**1b**	C_2H_5	H	76
3	**1c**	n-C_3H_7	H	84
4	**1d**	n-C_8H_{17}	H	95
5	**1e**	CH_2=$CH(CH_2)_7$	H	72
6	**1f**	n-C_9H_{19}	H	95
7	**1g**	n-$C_{16}H_{33}$	H	91
8	**1h**	CH_3	CH_3	87
9	**1k**	CH_3	CH_2=$CHCH_2$	79
10	**1j**	CH_3	n-C_3H_7	82
11	**1i**	CH_3	n-C_8H_{17}	95

from the initial attack of the first equivalent of organometallic reagent are possible, the major side reaction is normally the addition of a second equivalent of organometallic to form the tertiary alcohol. A variety of techniques have been developed to improve the synthesis of ketones from derivatives of carboxylic acids. These include the reaction of organolithium reagents with carboxylic acids or their salts[6] and the use of very reactive derivatives, notably acyl halides and acid anhydrides, with an array of organometallic reagents,[7] amides with organometallic reagents,[8] and nitriles with organometallic reagents.[9] In addition, the reaction of a Grignard reagent with esters

Scheme I



disposed to yield stable intermediates hydrolyzable to the ketone has met with success.[10]

Despite the attractiveness of the reaction of an organometallic reagent with the common ester group to give a ketone, this reaction has not met with general success,[11] although good results have been realized in certain sterically hindered cases[12] and when the reaction is carried out in the presence of a large excess of triethylamine.[13]

We reasoned that α-diphenylmethylsilyl esters, readily available from the parent esters,[14] should react with an organolithium or organomagnesium reagent to yield a β-keto silane that, due to the bulk of the diphenylmethylsilyl group, should be much less susceptible to nucleophilic attack.[12d] Protiodesilylation of the β-keto silane would complete the ester to ketone transformation (eq 1).[15]

Results and Discussion

Preparation of α-Silyl Esters. A brief study comparing methyl esters with ethyl esters revealed that the reaction proceeds without any significant differences, and we have therefore limited our study to the ethyl esters **1**. The preparation of the monosubstituted α-silyl esters **1**

(1) The chemistry of α-Silyl Carbonyl Compounds. 11. Presented in part at the following: 189th National Meeting of the American Chemical Society, St. Louis, MO, April 1984, ORGN 140; VIIth International Symposium on Organosilicon Chemistry, Kyoto, Japan, Sep 1984.

(2) MARC Faculty Fellow on leave from Bayamon Regional College. Taken in part from the Ph.D. Thesis of D.H., The University of Puerto Rico-Rio Piedras Campus, 1984.

(3) Graduate student funded on MBRS Grant RR-8102-10.

(4) MARC Predoctoral Trainee 1984–1987.

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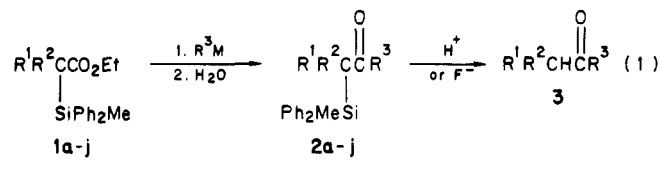
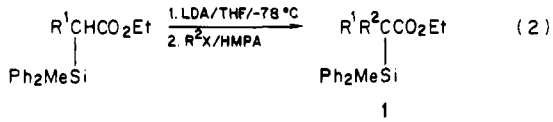


(1)

comp	R^1	R^2
a	CH_3	H
b	C_2H_5	H
c	C_3H_7	H
d	$-C_8H_{17}$	H
e	$CH_2{=}CH(CH_2)_7$	H
f	$-C_9H_{19}$	H
g	$-C_{16}H_{33}$	H
h	CH_3	CH_3
i	$-C_8H_{17}$	CH_3
j	$-C_3H_7$	CH_3
k	C_3H_5	CH_3

was accomplished uneventfully according to our published procedure.[14] The dialkylated derivatives **1** were prepared in good yield by alkylation of the monoalkylated α-silyl esters (eq 2).[16] The direct C-silylation of secondary esters does not occur without the concomitant or exclusive formation of the O-silylated isomer.[14,17] The results of these preparations are given in Table I.



(2)

General Considerations. It was quickly evident that unlike the α-silylacetates, **1**, (R^1, R^2 = H) the reaction of the monosubstituted derivatives with Grignard reagents is very slow.[18] The reaction requires a fourfold or greater excess of the Grignard reagent in refluxing THF and 17–72 h for completion. By way of comparison, ethyl decanoate reacted with methylmagnesium bromide under similar conditions to give 2-methyl-2-undecanol in 99% yield. As in our earlier work, the reaction of the α-silyl esters with organolithium reagents gives a synthetically useless mixture of compounds and the use of Grignard reagents prepared with high-purity magnesium provides the best results.

The reaction of a Grignard reagent with **1** could take several pathways. The most likely of these, shown in Scheme I, assumes the intermediacy of β-keto silane **2**.[19] Thus, when R^3 contains a β-hydrogen reduction of **2** to β-oxido silane **4**, which would lead to olefin **5** via an acid-catalyzed Peterson elimination is possible.[20] We have not observed any evidence for this pathway in our studies. β-Keto silane **2** could suffer nucleophilic attack by a second equivalent of Grignard reagent, producing β-oxido silane **6**, which would lead to olefin **7**. This, in fact, is the major competing pathway to that of the desired ketone synthesis.[21] Finally, **2** can be deprotonated when R^3 contains α-hydrogens to give enolate **8**, which would be inert to the reaction conditions and would protonate to the β-keto silane **2**.[22] Although deprotonation of the α-position containing the diphenylmethylsilyl moiety is possible in those cases where R^2 = H, we have not observed this reaction pathway in our studies, undoubtedly due to the steric hinderance imparted by the alkyl and the diphenylmethylsilyl groups.

Preparation of Ketones. Since our initial interest was to investigate the ester to α-silyl ester to ketone sequence and the viability of this two-step ester to ketone transformation, we did not concern ourselves with the isolation and characterization of the β-keto silanes **2**. In all of these systems, however, the crude reaction product from the reaction of **1** with the Grignard reagent showed a carbonyl absorbance in the infrared spectrum at approximately 1680–1695 cm^{-1}, consistent with those of a β-keto silane.[15a] This was often accompanied by an absorbance at ca. 1710 cm^{-1} for the desilylated ketone, resulting from the aqueous workup. The crude β-keto silane was protiodesilylated to the desired ketone with aqueous HCl in THF or with methanolic potassium fluoride, the latter giving the more consistent results and the shorter reaction times. The results are shown in Table II.

In our previous work we showed that the α-silylacetates **1** (R^1 = R^2 = H) undergo bis addition followed by elimination to give olefins **7**, except with hindered Grignard reagents, which do not react at all.[18] Thus, the presence of the diphenylmethylsilyl group alone is not sufficient to limit the reaction to a single addition. The presence of a methyl group together with the silyl group, however, gives a good yield of the ketone when a long-chain Grignard reagent is employed (entry 1). The yields are lower when methylmagnesium halides are reacted with monoalkylated esters (entries 3–5) and even with the dialkylated esters (entry 24). Methylmagnesium iodide requires longer reaction times than methylmagnesium bromide, which is slightly more reactive than methylmagnesium chloride. The combination of two long-chain units presents no problem as seen by the conversion of ethyl stearate to 17-tetratriacontanone (entry 17). The use of phenylmagnesium bromide results in slightly more olefin, most likely because enolization is not a viable possibility in these β-keto silanes (entry 15). Allylmagnesium bromide reacts with **1d** to give the corresponding olefin **7** (R^1 = C_8H_{17}, R^2 = H, R^3 = allyl) in 84% yield with no evidence for the ketone. Allylmagnesium chloride has been shown to add in a bis manner to α-chloro esters, whereas the reaction with other Grignard reagents can be moderately controlled to add a single equivalent.[11e]

The reaction of monoalkylated α-silyl esters with vinylmagnesium bromide proceeds to add 2 equiv of the Grignard reagent, leading to polymeric material after Peterson elimination. The dialkylated esters, on the other hand, give bis addition, but with the second equivalent adding in a Michael fashion (vide supra).[23]

It was felt that it should be possible to carry out the ester to ketone transformation directly without isolation and purification of the α-diphenylmethylsilyl ester. Thus, 60 mmol of ethyl decanoate was diphenylmethylsilylated; the crude reaction product was dissolved in THF and treated with propylmagnesium bromide and then sulfuric acid in THF to give a 60% yield, based on ethyl decanoate, of 4-tridecanone. In a similar reaction ethyl 10-undecenoate was reacted with ethylmagnesium bromide to give a 50%

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(18) Larson, G. L.; Hernandez, D. *Tetrahedron Lett.* **1982**, *23*, 1035.
(19) This work has been communicated: Larson, G. L.; Montes de Lopez-Cepero, I.; Torres, L. E. *Tetrahedron Lett.* **1984**, *25*, 19.
(20) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464 and references therein.
(21) For the synthesis of tri- and tetrasubstituted olefins from α-silyl esters consult: Larson, G. L.; Hernandez, D. *J. Org. Chem.* **1984**, *49*, 4285.
(22) For an example of this consult ref 12d. The regioselective deprotonation of β-keto silanes has been reported: Kuwajima, I.; Inoue, T.; Sato, T. *Tetrahedron Lett.* **1978**, 4887.
(23) (a) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 146–149. (b) Brook, A. G.; MacRae, D. M.; Limburg, W. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493. (c) Lutsenko, I. F.; Baukov, Yu. I.; Kostyuk, A. S.; Savalyeva, N. I.; Krysina, V. K. *J. Organomet. Chem.* **1969**, *17*, 241. (d) Brook, A. G.; MacRae, D. M.; Bassindale, A. R. *Ibid.* **1975**, *86*, 185. (e) Larson, G. L.; Fernandez, Y. V. *Ibid.* **1975**, *86*, 193. (f) Kwart, H.; Barnett, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 614.

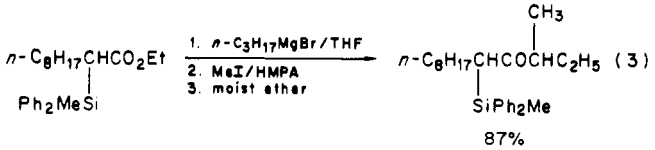
Table II. Ketones from α-Diphenylmethylsilyl Esters

entry	ester	R^3	X	olefin,[a,b]	ketone,[a,b]
1	**1a**	n-C_9H_{19}	Br		3-dodecanone (71)[c]
2	**1a**	n-C_3H_7	Br	*d*	3-hexanone (55)[e]
3	**1d**	CH_3	I	2-methyl-2-undecene (45)[f]	2-undecanone (55)[g]
4	**1d**	CH_3	Br	*d*	2-undecanone (58)
5	**1d**	CH_3	Cl	*d*	2-undecanone (42)
6	**1d**	C_2H_5	I	3-ethyl-3-dodecene (9)	3-dodecanone (71)
7	**1d**	C_2H_5	Br	*d*	2-methyl-3-dodecanone (58)[h]
8	**1d**	n-C_3H_7	Br	4-propyl-7-tridecene (8)	4-tridecanone (78)[i]
9	**1d**	n-C_3H_7	Br	*d*	4-tridecanone (60)[j]
10	**1d**	n-C_3H_7	Br	*d*	3-methyl-5-(diphenylmethylsilyl)-4-tridecanone (87) (see Table III)
11	**1d**	n-C_6H_{13}	Br	7-hexyl-7-hexadecene (8)	7-hexadecanone (56)[k]
12	**1d**	n-C_9H_{19}	Br		10-nonadecanone (70)[l]
13	**1d**	n-$C_{13}H_{27}$	Br		10-trieicosanone (64)[m]
14	**1d**	$PhCH_2$	Cl		1-phenyl-2-undecanone (65)[n]
15	**1d**	Ph	Br	1,1-diphenyl-1-decene (20)[n]	1-phenyl-1-decanone (58)[o]
16	**1d**	C_2H_5	I	11-ethyl-1,10-tridecadiene (5)	11-tridecen-3-one (85)[p]
17	**1g**	n-$C_{16}H_{31}$	Br		17-tetratriacontanone (58)
18	**1g**	n-$C_{15}H_{31}$	Br		15-methyl-16-tritriacontanone (73)[h]
19	**1h**	n-C_6H_{13}	Br	3-hexyl-2-methyl-2-nonene (44)	2-methyl-3-nonanone (22)
20	**1h**	n-C_9H_{19}	Br		2-methyl-3-dodecanone (76)
21	**1h**	$PhCH_2$	Cl		1-phenyl-3-methyl-2-butanone (67)[q]
22	**1h**	C_2H_3	Br		2-methyl-6-hepten-3-one (75)
23	**1h**	C_2H_3	Br		4,6-dimethyl-1-hepten-5-one (75)[h]
24	**1i**	CH_3	I	2,3-dimethyl-2-undecene (12)	3-methyl-2-undecanone (53)
25	**1i**	C_2H_5	Br		4-methyl-3-dodecanone (94)[r]
26	**1i**	C_2H_3	Br		6-methyl-1-tetradecen-5-one (87)
27	**1j**	C_2H_5	Br		4-methyl-3-heptanone (79)[s]
28	**1h**	C_2H_3	Br		4-methyl-1,8-nonadien-5-one (67)
29	**1k**	n-C_4H_9	Br		4-methyl-1-nonen-5-one (74)
30	**1h**	$(CH_3)_2C{=}CH_2$	Br		2,4,4,7-tetramethyl-2-octen-6-one (42)[t]

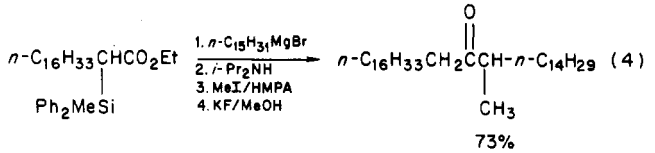
[a] Isolated yields. Products purified by silica gel chromatography or flash distillation. Final purification in some cases was done by preparative GLC on a 3 ft × 14 in. SE-30 column. [b] Spectral and some physical data are given in the Experimental Section or the supplementary material. [c] For an ^1H NMR spectrum of an authentic sample consult: Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1978**, *43*, 2907. [d] Not determined. [e] IR identical with that of an authentic sample: Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 3rd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1981; p 241F. [f] n^{20}_D 1.4360; lit. n^{20}_D 1.4350: Beilstein, *Part 3* **1974**, *1*, 916. [g] IR identical with that of an authentic sample: Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 3rd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1981; p 245E. [h] Formed by the addition of iodomethane/HMPA to the reaction prior to workup. [i] n^{20}_D 1.4410; lit. n^{20}_D 1.4105: *Beilstein, Part 5* 1974, *1*, 3387. [j] Reaction carried out on a 50-mmol scale without purification of the α-silyl ester, **1c**. The yield is based on ethyl decanoate. [k] n^{20}_D 1.4276; lit. n^{20}_D 1.4280: *Beilstein, Part 5* **1974**, *1*, 3394. [l] IR identical with that of an authentic sample: Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 3rd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1981; p 246B. [m] mp 60–61 °C; lit. mp 60.6–61.6 °C: Baykut, O. *Rev. Fac. Sci. Istanbul C* **1956**, *21*, 102, 104, 106. [n] ^1H NMR and IR spectra were identical with those published: Grant, D. W.; Shitton, R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 135. [o] ^1H NMR spectrum identical with that of an authentic sample: Poucert, C. J. "The Aldrich Library of NMR Spectra", 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1983; Vol. 2, p 98. [p] Reaction carried out on a 50-mmol scale without purification of **1d** gave the ketone in 50% yield based on ethyl 10-undecenoate. [q] n^{20}_D 1.5025; lit. n^{20}_D 1.5040: Nielson, A.; Gibbons, C.; Zimmerman, C. A. *J. Am. Chem. Soc.* **1951**, *73*, 4696. [r] n^{20}_D 1.4357; lit. n^{20}_D 1.4313; Allen, J. C.; Cadogan, J.; Hey, D. H. *J. Chem. Soc.* **1965**, 1918. [s] n^{20}_D 1.4145; lit. n^{20}_D 1.4137: Dubois, J.; Luft, R. *Bull. Soc. Chim. Fr.* **1954**, 1153. [t] Obtained from protiodesilylation of **13**. See eq 6.

yield of tridec-11-en-3-one. The direct conversion of an ester to a ketone is therefore possible without purification of the intermediate α-silyl ester, although the yields suffer somewhat.

In order to check for the formation of the enolate **8**, ester **1d** was reacted with ethylmagnesium bromide and the reaction mixture treated with a threefold excess of iodomethane. This gave, after protiodesilylation, a mixture of 2-methyl-3-dodecanone (58%) and 3-dodecanone (36%). Better results were obtained when this same ester was treated sequentially with propylmagnesium bromide, a fivefold excess of iodomethane, and potassium fluoride in methanol, to provide 3-methyl-4-(diphenylmethylsilyl)-4-tridecanone in 87% yield (eq 3). Clearly, the enolate **8**



is formed in the reaction and, as expected, in a regioselective manner. This regiospecific methylation is even possible with long-chain systems as shown in entry 18 wherein the reaction mixture was treated with diisopropyl amine after the reaction with pentadecylmagnesium bromide had terminated to ensure complete deprotonation and avoid purification problems and then a fivefold excess of iodomethane to give a 73% yield of 15-methyl-16-tritriacontanone (eq 4).



Preparation of β-Keto Silanes. β-Keto silanes have been prepared in several ways, none of which are both general and straightforward. Synthetically they have proven themselves as worthy precursors to olefins[24] and substituted ketones as well as for the versatile enol silyl ethers.[25] They are, however, prone to solvolytic protiod-

(24) For examples of this consult: (a) Fujita, T.; Watanabe, S.; Suga, K.; Yokoyama, T. *Yukagaku* **1977**, *26*, 429; *Chem. Abstr.* **1977**, *87*, 184046*v*. (b) Suga, K.; Fujita, T.; Watanabe, S.; Takahasi, Y. *Synthesis* **1974**, 133.

(25) (a) Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1972**, 1785. (b) Utimoto, K.; Obayashi, M.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2940. (c) Obayashi, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1977**, 1807.

Table III. Preparation of β-Keto Silanes

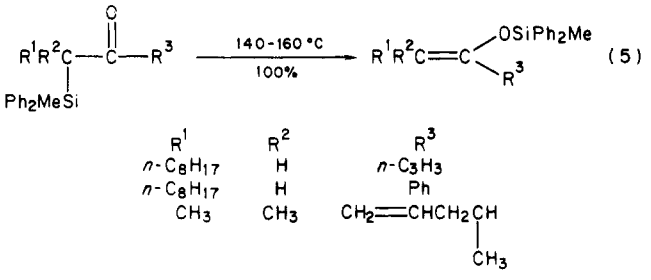
entry	ester	R^3MgX	product[a] R^1	R^2	R^3		% yield[b]
1	1d	CH_3MgBr	n-C_8H_{17}	H	CH_3	2a	71
2	1d	n-C_3H_7MgBr	n-C_8H_{17}	H	n-C_3H_7	2b	93
3	1d	n-C_3H_7MgBr	n-C_8H_{17}	H	$CH_3CH_2CH(CH_3)$[d]	2c	87
4	1d	n-$C_9H_{19}MgBr$	n-C_8H_{17}	H	n-C_9H_{19}	2d	97[e]
5	1d	n-$C_{13}H_{27}MgBr$	n-C_8H_{17}	H	n-$C_{13}H_{27}$	2e	95[f]
6	1d	PhMgBr	n-C_8H_{17}	H	Ph	2f	82[c]
7	1h	CH_2=$CHMgBr$	CH_3	CH_3	CH_2=$CHCH_2CH_2$	2g	78
8	1h	CH_2=$CHMgBr$	CH_3	CH_3	CH_2=$CHCH_2CH(CH_3)$	2h	75[d]
9	1h	$(CH_3)_2C$=$CHMgBr$	CH_3	CH_3	see eq 6	2i	42
10	1k	CH_2=$CHMgBr$	CH_3	C_3H_5	CH_2=$CHCH_2CH_2$	2j	70

[a] According to eq 1. [b] Isolated yields. [c] Contaminated with a small amount of the olefin. [d] Reaction quenched with iodomethane/HMPA prior to workup. [e] Product is about 96% pure. [f] Contaminated with tridecane from protonation of the excess Grignard reagent.

esilylation and thermal rearrangement.

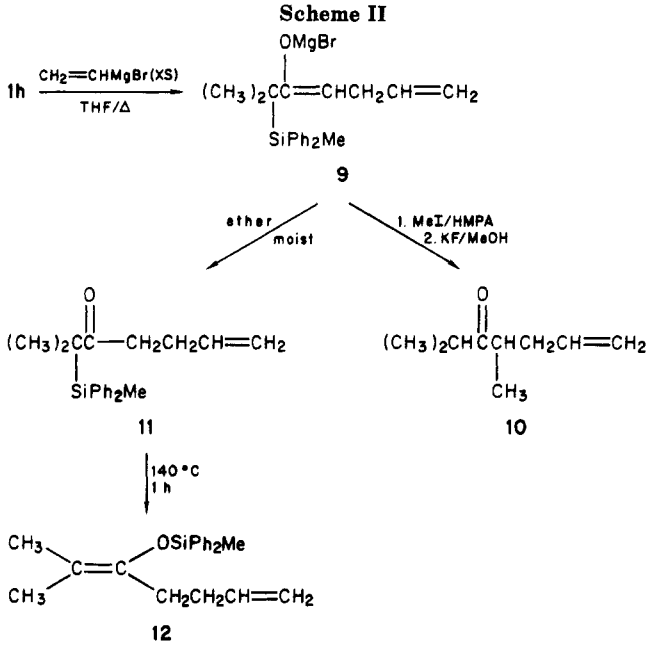
Initially, the purification of the β-keto silanes **2** proved to be a serious problem. Distillation required temperatures well above 100 °C and resulted in isomerization to the enol silyl ethers. Furthermore, chromatography on silica gel, Florisil, or alumina resulted in protiodesilylation. Moreover, standard aqueous workup of the reaction gave partial and, at times, complete desilylation of **2**. Fortunately, it was found that hydrolysis of the reaction by careful addition of moist ether and then anhydrous sodium sulfate gave a semicrystalline solid in the bottom of the solution. Simple decantation of the solution and washing of the solid with ether resulted in an organic phase free of salts. Concentration of this organic solution provided the β-keto silane with a minimum of desilylation. Purification by chromatography is best accomplished with a silica gel column, which has been pretreated with triethylamine/ethyl acetate/hexane (0.5:1.5:98), eluting with this same solvent mixture. All such purified β-keto silanes were at least 95% pure. The results are shown in Table III. As expected the yields are lower in the less hindered cases. It also turns out that, in general, the more substituted systems are less readily desilylated.

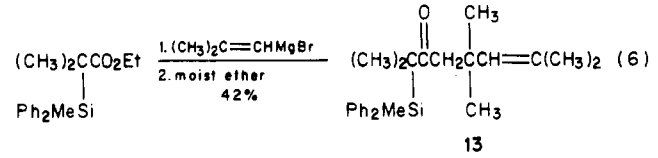
It is possible to take advantage of the well-known thermal β-keto silane to enol silyl ether rearrangement to regioselectivity prepare enol silyl ethers (eq 5).[15a] This represents a potentially very useful and general entry into regioselectively defined enol silyl ethers.



The addition of vinylmagnesium bromide to **1h** gives enolate **9**, which can be methylated and desilylated to ketone **10** (Table II, entry 22) or protonated to β-keto silane **11**. Isomerization of **11** produces enol silyl ether **12** in quantitative yield (Scheme II). In an attempt to prepare an α,β-unsaturated ketone, **1h** was treated with (2-methyl-1-propenyl)magnesium bromide. This, surprisingly, also lead to Michael addition of the second equivalent of Grignard reagent, producing β-keto silane **13** in 42% yield (eq 6).

Scheme II



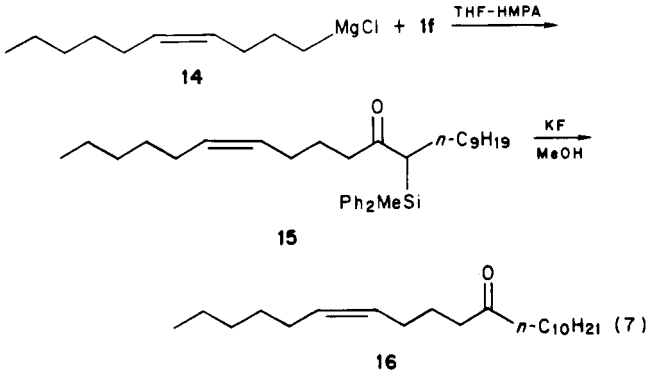


Synthesis of the Douglas Fir Tussock Moth Pheromone. The Douglas fir tussock moth (orygia *Pseudotsugata*) is a despoiler of the forests of western North America, making its control of paramount economic concern. Although a variety of syntheses of (*Z*)-6-heneicosen-11-one (**16**), the active component of the sex pheromone of this pest, have been reported,[27] the methodology presented here for the ester to ketone transformation provides an extremely efficient, two-step preparation of **16** from readily available starting materials.

(26) For excellent reviews on the chemistry of enol silyl ethers consult: (a) Colvin, E. "Silicon in Organic Synthesis"; Butterworths: Boston, MA, 1981; Chapter 17. (b) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: New York, 1983; Chapters 12–16. (c) Brownbridge, P. *Synthesis* **1983**, 1 and 85.

(27) (a) Wang, K. K.; Chu, K.-H. *J. Org. Chem.* **1984**, *49*, 5175. (b) Nishiyama, H.; Sakuta, K. Itoh, K. *Tetrahedron Lett.* **1984**, *25*, 223. (c) Trost, B. M.; Ornstein, P. L. *Ibid.* **1981**, *22*, 3463. (d) Zweifel, G.; Pearson, N. *J. Am. Chem. Soc.* **1980**, *102*, 5919. (e) Cahiez, G.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1980**, *21*, 1433. (f) Vig, O. P.; Sharma, M. L.; Verma, N. K.; Malik, N. *Ind. J. Chem.* **1980**, *19B*, 950. (g) Fetizon, M.; Lazare, C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 842. (h) Akermark, B.; Ljungvist, A. *J. Org. Chem.* **1978**, *43*, 4387. (i) Mori, K.; Uchida, M.; Matsui, M. *Tetrahedron* **1977**, *33*, 385. (j) Smith, R. J.; Daves, G. D., Jr.; Daterman, G. E. *J. Org. Chem.* **1975**, *40*, 1593. (k) Sokolovska, S. V. *Khim. Prir. Soedin.* **1980**, *102*; *Chem. Abstr.* **1980**, *93*, 45902g.

Secure in the fact that the reaction of α-diphenylmethylsilyl esters with long-chain Grignard reagents proceeds well, we were surprised to find that refluxing the Grignard reagent of (*Z*)-1-chloro-4-decene[28] (**14**) with **1k** in THF for 3 days gave no reaction. Similar results were obtained in refluxing THF/ether, THF/DME, THF/toluene, and THF with added potassium *tert*-butoxide. It was not until 2.4 equiv of HMPA was added to the THF solvent system that the desired reaction occurred. We speculatively attribute this lack of reactivity to steric crowding resulting from the *Z* geometry of the Grignard reagent. Direct protiodesilylation of the crude β-keto silane **15** produced the pheromone **16** in 80% yield. Although β-keto silane **15** was formed in greater than 90% yield, it was not possible to purify it without concomitant protiodesilylation (eq 7).



(7)

Conclusions. The ready α-silylation of esters via their lithium enolates provides an excellent route to α-silyl esters, which can be reacted with Grignard reagents to yield β-keto silanes and ketones. This not only provides a rather general entry into β-keto silanes but also a highly useful two-step conversion of esters into ketones, a functional group transformation only open to highly hindered ketones to date. Moreover the β-keto silanes represent excellent precursors to regiospecifically defined enol silyl ethers.

Experimental Section

General Considerations. The standard apparatus consists of a round-bottomed, three-necked flask equipped with a dropping funnel, reflux condenser, and a no-air septum. This apparatus was either dried in an oven at 120 °C for a minimum of 4 h or flame-dried and then cooled under an atmosphere of nitrogen. All reactions were carried out under an atmosphere of predried nitrogen. Room temperature is approximately 30 °C. Grignard reagents were prepared by accepted procedures in ether or THF. Ether and THF were distilled from benzophenone ketyl prior to use. Esters and organic halides were purchased from Aldrich Chemical Co. and were distilled prior to use. Diphenylmethylchlorosilane (Petrarch Systems, Inc.) was distilled from calcium hydride prior to use. THF solutions of lithium diisopropylamide (LDA) were prepared by adding a titrated hexane solution of *n*-butyllithium to an equal amount of THF at −78 °C, adding an equivalent amount of diisopropylamine in THF, and stirring for 15 min at room temperature followed by recooling to −78 °C. The solvents employed for chromatography were mixed in volume percentages. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as neat liquid films unless otherwise noted. Nuclear magnetic resonance spectra (^1H, ^{13}C) were recorded on a Jeol FX90Q spectrometer as solutions in chloroform-*d* and are recorded in ppm with respect to internal tetramethylsilane for all nuclei. Mass spectra were recorded on Hewlett-Packard 5995A or 5987 spectrometers and are recorded as *m/e* (relative intensity).

Preparation of α-Diphenylmethylsilyl Esters. General Procedure. Following our general procedure,[14] 55 mmol of LDA was prepared in a 500-mL standard apparatus and 70 mL of THF was added followed by the addition of 52 mmol of the ester in 50 mL of THF. This solution was stirred at −78 °C for 30 min, the enolate was quenched by the dropwise addition of 52 mmol of diphenylmethylchlorosilane in 20 mL of THF, and the solution was allowed to reach room temperature where it was stirred overnight. The reaction mixture was then diluted with hexane (100 mL) and washed with cold water (3 × 25 mL). The organic layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure. The crude product, which was generally greater than 95% pure, was purified by silica gel chromatography, eluting with 2–3% ethyl aceate/hexane or alternatively by Kugelrohr distillation.

Ethyl 2-(Diphenylmethylsilyl)propionate (1a). A 52-mmol scale reaction and chromatography gave 12.9 g (83%) of the title ester, whose properties have been reported.[14]

Ethyl 2-(Diphenylmethylsilyl)butyrate (1b). A 50-mmol reaction and chromatography gave 11.8 g (76%) of the title ester: n^{20}_D 1.5374; IR 1710 cm^{-1}; ^1H NMR δ 7.26–7.61 (m, 10 H), 3.84 (q, 2 H, *J* = 7.1 Hz), 2.50 (m, 1 H), 1.50–1.80 (m, 2 H), 1.19 (t, 3 H), 0.93 (t, 3 H, *J* = 7.1 Hz), 0.65 (s, 3 H); ^{13}C NMR δ 174.6, 134.8, 134.2, 129.4, 127.7, 59.6, 38.5, 21.1, 14.9, 14.0, −5.5; MS 314 (3), 313 (10), 312 (35), 297 (26), 269 (13), 267 (11), 235 (11), 227 (21), 207 (22), 197 (100), 191 (11), 165 (22), 137 (12), 121 (6), 105 (13), 55 (6), 41 (4).

Ethyl 2-(Diphenylmethylsilyl)pentanoate (1c). A 20-mmol scale reaction and Kugelrohr distillation gave 5.5 g (84%) of the title ester: n^{20}_D 1.5342; IR 1710 cm^{-1}; ^1H NMR δ 7.66–7.28 (m, 10 H), 3.99–3.66 (m, 2 H, diastereotopic methylenes), 2.55 (m, 1 H), 1.48–1.15 (m, 4 H), 0.93 (t, 3 H, *J* = 7.0 Hz), 0.87 (br t, 3 H), 0.66 (s, 3 H); ^{13}C NMR δ 175.0, 134.7, 133.9, 129.4, 127.7, 59.7, 36.0, 29.5, 23.5, 13.9, 13.6, −5.7; MS 326 (4), 197 (100), 165 (29), 137 (37), 121 (30), 119 (23), 105 (70), 77 (20), 55 (64), 45 (23), 43 (27). Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 73.62; H, 7.98. Found: C, 73.46; H, 8.05.

Ethyl 2-(Diphenylmethylsilyl)decanoate (1d). A 50-mmol scale reaction and chromatography gave 18.8 g (95%) of the title ester: n^{20}_D 1.5190; IR 1710 cm^{-1}; ^1H NMR δ 7.62–7.29 (m, 10 H), 4.04–3.68 (m, 2 H, diastereotopic methylenes), 2.49–2.63 (m, 1 H), 1.21 (br s, 14 H), 0.95 (t, 3 H, *J* = 7.1 Hz), 0.83 (br t, 3 H), 0.66 (s, 3 H); ^{13}C NMR δ 175.0, 134.8, 134.4, 129.5, 127.8, 59.7, 36.4, 31.9, 30.5, 29.2, 27.6, 22.6, 14.0, −5.5; MS 398 (10) 397 (19), 396 (33), 353 (21), 351 (20), 319 (27), 298 (39), 297 (75), 284 (23), 227 (33), 199 (30), 198 (43), 197 (100), 195 (30), 183 (26), 181 (27), 121 (35), 105 (39), 93 (20), 73 (24), 69 (21), 55 (36), 53 (16). Anal. Calcd for $C_{25}H_{36}O_2Si$: C, 75.76; H, 9.09. Found: C, 75.59; H, 9.19.

Ethyl 2-(Diphenylmethylsilyl)-10-undecenoate (1e). A 25-mmol scale reaction and chromatography gave 7.3 g (72%) of the title ester: n^{20}_D 1.5700; IR 1715, 1640 cm^{-1}; ^1H NMR δ 7.80–7.25 (m, 10 H), 6.19–5.52 (m, 1 H), 5.11–4.84 (m, 2 H), 3.95 (q, 2 H, *J* = 7.18 Hz), 2.48 (m, 2 H), 2.00 (m, 1 H), 1.21 (s, 12 H), 0.93 (t, 3 H, *J* = 7.18 Hz), 0.65 (s, 3 H); ^{13}C NMR δ 175.0, 139.0, 134.7, 134.2, 129.5, 127.7, 114.0, 59.7, 36.2, 34.3, 33.7, 30.4, 29.1, 29.0, 28.8, 27.4, 13.9, −5.7; MS 408 (1), 298 (20), 227 (10), 198 (18), 197 (100), 165 (23), 137 (15), 105 (14), 73 (7), 55 (24). Anal. Calcd for $C_{26}H_{36}O_2Si$: C, 76.47; H, 9.31. Found: C, 76.20; H, 9.35.

Ethyl 2-(Diphenylmethylsilyl)undecanoate (1f). In a manner similar to that above, 1.4 g (6.5 mmol) of ethyl undecanoate was converted to its enolate anion and this quenched with 1.51 g (6.5 mmol) of diphenylmethylchlorosilane to give, after concentration and silica gel chromatography, eluting with hexane/ethyl acetate (98:2), 5.6 g (90%) of **1f**, which was approximately 96% pure and showed n^{20}_D 1.5029: IR 1722 cm^{-1}; ^1H NMR δ 7.5–7.3 (m, 10 H), 3.85 (m, 2 H), 2.49 (m, 1 H), 1.23 (m, 16 H), 0.94 (t, 6 H, *J* = 7.1 Hz), 0.65 (s, 3 H); ^{13}C NMR δ 175.1, 134.8, 134.6, 134.3, 129.5, 127.9, 127.7, 59.7, 36.3, 31.9, 30.5, 29.5, 29.4, 29.3, 27.5, 22.6, 14.0, −5.1; MS 410 (6), 197 (100).

Ethyl 2-(Diphenylmethylsilyl)stearate (1g). A solution of 30 mmol of LDA was prepared in 40 mL of THF/hexane and cooled to −78 °C and 7.8 g (25 mmol) of ethyl stearate diluted in 300 mL of THF added over a 4-h period. The resulting solution was stirred an additional 1.5 h at this temperature and quenched with 10.3 g (50 mmol) of diphenylmethylchlorosilane. The temperature was allowed reach room temperature and was stirred at that temperature overnight. Standard workup and chromatography on silica gel deactivated with 10% triethylamine/

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methanol gave 11.9 g (91%) of the title ester, which was 96% pure: n^{20}_D 1.5094; IR 1715 cm^{-1}; ^{1}H NMR δ 7.5–7.1 (m, 10 H), 4.1–3.5 (m, 2 H, diastereotopic methylenes), 2.38–2.36 (m, 1 H), 1.8–1.1 (br s, 31 H), 0.8 (t, 3 H, J = 7 Hz), 0.53 (s, 3 H); ^{13}C NMR δ 174.7, 134.6, 133.8, 127.7, 127.5, 59.5, 36.2, 31.8, 30.4, 29.6, 14.0, 13.8, –5.7.

Ethyl 2-(Diphenylmethylsilyl)-2-methylpropionate (1h). A solution of 15.5 mmol of LDA in hexane/THF was reacted with 15 mmol of **1a** at –78 °C for 30 min, after which time 0.9 mL (5 mmol) of HMPA was added followed by the addition of 0.96 mL (15.5 mmol) of iodomethane. The solution was allowed to reach room temperature where it was stirred overnight. The organic layer was washed with 10% sodium sulfate (2 × 15 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvents were removed under reduced pressure. The resulting crude product was purified by Kugelrohr distillation to give 4.1 g (87%) of the title ester: n^{20}_D 1.5527; IR 1708 cm^{-1}; ^{1}H NMR δ 7.66–7.28, (m, 10 H), 3.93 (q, 2 H, J = 7.1 Hz), 1.32 (s, 6 H), 1.00 (t, 3 H, J = 7.1 Hz), 0.68 (s, 3 H); ^{13}C NMR δ 178.0, 135.2, 134.4, 129.4, 127.6, 60.1, 32.6, 22.2, 13.9, –5.3; MS 314 (2), 313 (7), 312 (27), 207 (12), 199 (9), 198 (17), 197 (100), 191 (12), 165 (12), 137 (19), 121 (7), 119 (7), 105 (19), 70 (16), 43 (3), 41 (4). Anal. Calcd for $C_{19}H_{24}O_2Si$: C, 73.08; H, 7.69. Found: C, 73.25; H, 7.77.

Ethyl 2-(Diphenylmethylsilyl)-2-methyldecanoate (1i). Following the general methylation procedure above, 4.75 g (12 mmol) of **1d** gave 4.6 g (95%) of the title ester: n^{20}_D 1.5202; IR 1710 cm^{-1}; ^{1}H NMR δ 7.69–7.49 (m, 4 H), 7.36–7.27 (m, 6 H), 3.93 (q, 2 H, J = 7.1 Hz), 1.28 (s, 3 H), 1.22 (br s, 14 H), 1.02 (t, 3 H, J = 7.1 Hz), 0.86 (t, 3 H), 0.68 (s, 3 H); ^{13}C NMR δ 177.0, 135.3, 134.7, 129.2, 127.5, 59.9, 37.1, 34.9, 31.7, 29.9, 29.3, 29.1, 24.7, 22.5, 17.6, 13.9, –5.3; MS 411 (6), 410 (7), 311 (46), 197 (100), 165 (14), 137 (12), 119 (10), 112 (20), 105 (17), 69 (47), 55 (17), 43 (33), 41 (35). Anal. Calcd for $C_{26}H_{38}O_2Si$: C, 76.09; H, 9.27. Found: C, 75.95; H, 9.33.

Ethyl 2-(Diphenylmethylsilyl)-2-methylpentanoate (1j). Following the general methylation procedure above, 12 mmol of **1c** and chromatography gave 3.3 g (82%) of the title ester: n^{20}_D 1.5373; IR 1710 cm^{-1}; ^{1}H NMR δ 7.69–7.20 (m, 10 H), 3.93 (q, 2 H, J = 7.3 Hz), 1.42 (m, 4 H), 1.27 (s, 3 H), 1.03 (t, 3 H, J = 7.3 Hz), 0.85 (m, 3 H), 0.68 (s, 3 H); ^{13}C NMR δ 176.8, 135.3, 133.9, 129.3, 127.6, 59.7, 37.1, 17.8, 17.5, 14.3, 13.8, –5.2; MS 341 (2), 340 (7), 311 (14), 205 (17), 197 (100), 165 (13), 105 (24), 98 (19), 69 (50), 41 (24). Anal. Calcd for $C_{22}H_{28}O_2Si$: C, 74.11; H, 8.23. Found: C, 73.98; H, 8.32.

Ethyl 2-(Diphenylmethylsilyl)-2-methylpent-5-enoate (1k). Following the general methylation procedure above and substituting allyl bromide for iodomethane, 20 mmol of **1a** gave 5.4 g (79%) of the title ester after chromatography: n^{20}_D 1.5426; IR 1710, 1640 cm^{-1}; ^{1}H NMR δ 7.69–7.55 (m, 4 H), 7.32–7.25 (m, 6 H), 5.91–5.45 (m, 1 H), 5.02–4.84 (m, 2 H), 3.89 (q, 2 H, J = 7.1 Hz), 2.95 (dd, 1 H, J = 5.4, 13.6 Hz), 1.11 (dd, 1 H, J = 7.9, 13.6 Hz), 1.28 (s, 3 H), 0.96 (t, 3 H, J = 7.1 Hz), 0.68 (s, 3 H); ^{13}C NMR δ 176.5, 135.8, 134.4, 134.3, 129.5, 127.7, 117.7, 60.1, 39.5, 37.0, 17.8, 14.0, –5.2; MS 338 (not observed), 227 (5), 215 (4), 214 (20), 200 (18), 199 (100), 197 (4), 183 (5), 152 (4), 137 (20), 121 (6), 91 (9), 78 (7), 77 (20), 51 (7). Anal. Calcd for $C_{21}H_{26}O_2Si$: C, 74.56; H, 7.69. Found: C, 74.45; H, 7.78.

3-(Diphenylmethylsilyl)-2-undecanone (2a). A standard apparatus was charged with 2.9 mL of 2.75 M (8.0 mmol) of methylmagnesium bromide in ether, and 0.79 g (2.0 mmol) of **1d** in 10 mL of THF was added at 0 °C. The reaction mixture was heated to reflux for 58 h and cooled to room temperature, and then moist ether (25 mL) was added with stirring. The organic layer was removed by syringe, and the salts were washed with ether (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered, and the solvents were removed under reduced pressure. Silica gel chromatography as above gave 0.52 g (71%) of the title ketone of 96% purity: n^{20}_D 1.5125; IR 1690 cm^{-1}; ^{1}H NMR δ 7.7–7.3 (m, 10 H), 2.4–2.2 (m, 1 H), 2.1 (s, 3 H), 1.7–1.5 (m, 1 H), 1.3–0.75 (m, 17 H), 0.7 (s, 3 H); ^{13}C NMR δ 210.2, 134.6, 134.3, 133.9, 129.7, 127.8, 47.8, 32.5, 31.8, 30.7, 29.3, 27.7, 22.6, 14.0, –6.2; MS 336 (14), 197 (100), 137 (70).

5-(Diphenylmethylsilyl)-4-tridecanone (2b). Following the above procedure, 8 mmol of **1d** and 32 mmol of propylmagnesium bromide gave 2.94 g (93%) of the title ketone: n^{20}_D 1.5278; IR 1690 cm^{-1}; ^{1}H NMR δ 7.63–7.25 (m, 10 H), 2.99–2.37 (m, 3 H), 1.94–1.86 (m, 2 H), 1.79–1.67 (m, 2 H), 1.19–1.04 (m, 18 H), 0.63 (s, 3 H); ^{13}C NMR δ 212.3, 135.0, 134.7, 134.3, 129.7, 127.9, 47.5, 46.6, 31.8, 30.8, 29.4, 27.8, 22.7, 16.9, 14.1, 13.6, –6.2; MS 394 (1), 197 (63), 137 (100). Anal. Calcd for $C_{26}H_{38}OSi$: C, 79.12; H, 9.71. Found: C, 79.02; H, 9.76.

5-(Diphenylmethylsilyl)-3-methyl-4-tridecanone (2c). After the reaction above was carried out on a 2-mmol scale, the reaction mixture was cooled to room temperature and 0.1 mL of HMPA added, followed by the addition of 0.25 mL (4 mmol) of iodomethane. The standard workup gave 0.72 g (87%) of the title ketone of greater than 95% purity: n^{20}_D 1.5249; IR 1690 cm^{-1}; ^{1}H NMR δ 7.6–7.1 (m, 10 H), 3.0–2.0 (m, 3 H), 1.9–1.8 (m, 4 H), 1.4–0.72 (m, 18 H), 0.63 (s, 3 H); ^{13}C NMR δ 211.9, 134.9, 134.7, 133.9, 129.6, 127.9, 127.6, 47.4, 41.7, 31.8, 30.8, 29.3, 27.7, 22.6, 16.9, 16.7, 14.7, 14.0, 13.5, –6.3; MS 408 (16), 197 (100), 137 (72).

9-(Diphenylmethylsilyl)-10-nonadecanone (2d). The reaction of 1.98 g (5 mmol) of **1d** with 20 mmol of nonanylmagnesium bromide gave, after silica gel chromatography eluting with ethyl acetate/triethylamine/hexane (2:0.5:97.5), 2.32 g (97%) of product, which was about 90% pure. The contaminants were nonane and octadecane. This material showed IR 1695 cm^{-1}; ^{1}H NMR δ 7.5–7.2 (m, 10 H), 2.85 (m, 3 H), 1.8 (m, 4 H), 1.0 (br s, 27 H), 0.65 (br t, 6 H); ^{13}C NMR δ 212.3, 135.0, 134.6, 129.6, 128.0, 127.9, 46.6, 39.3, 31.9, 30.8, 30.3, 29.6, 29.3, 27.8, 23.5, 22.7, 14.1, –6.3; MS 478 (14), 197 (71), 137 (100).

9-(Diphenylmethylsilyl)-10-trieicosanone (2e). Following the procedure above, 5 mmol of **1d** was reacted with tridecanylmagnesium bromide to give greater than 95% of the title ketone contaminated with tridecane, which proved impossible to completely remove without decomposition of the β-keto silane: ^{1}H NMR δ 7.6–7.2 (m, 10 H), 2.5–2.3 (m, 3 H), 1.8–1.6 (m, 4 H), 1.3–0.7 (m, 39 H); ^{13}C NMR δ 211.8, 134.7, 134.3, 134.0, 129.6, 128.0, 127.7, 46.7, 32.1, 29.9, 29.5, 27.8, 23.5, 22.8, 14.1, 11.4, –6.3.

2-(Diphenylmethylsilyl)-1-phenyl-1-decanone (2f). The reaction of 0.79 g (5 mmol) of **1d** with 8 mmol of phenylmagnesium bromide gave a crude product that was purified by low-temperature (0–15 °C) silica gel chromatography, eluting with ethyl acetate/triethylamine/hexane (2:0.5:97.5). This yielded 0.70 g (82%) of the title compound that contained a small amount of the olefin 1,1-diphenyl-1-decene: n^{20}_D 1.5576; IR 1660 cm^{-1}; ^{1}H NMR δ 7.6–7.2 (m, 15 H), 2.45 (m, 1 H), 1.6 (m, 2 H), 1.2–0.8 (m, 15 H), 0.6 (s, 3 H); ^{13}C NMR δ 202.8, 135.1, 134.8, 134.6, 133.8, 129.4, 128.8, 128.6, 127.8, 127.6, 127.0, 126.5, 126.0, 125.4, 31.7, 30.8, 30.5, 29.5, 29.2, 28.8, 28.6, 28.3, 22.5, 14.0, –5.6; MS 428 (12), 251 (22), 197 (100), 155 (37), 137 (44).

6-(Diphenylmethylsilyl)-6-methyl-1-hepten-5-one (2g). A standard apparatus of 25-mL volume was charged with 20 mL of a 0.84 M (16.7 mmol) solution of vinylmagnesium bromide in THF and then 1.25 g (4 mmol) of **1h** in 4 mL of THF. The reaction mixture was heated to reflux for 17 h and cooled to 0 °C, and 150 mL of moist ether was added with stirring. The solids were allowed to settle. The solution was removed from the solids via syringe, and the solids were washed with ether (2 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate. After solvent removal at reduced pressure, the product was purified by silica gel chromatography, eluting with triethylamine/ethyl acetate/hexane (0.5:1.5:98) to give 1.0 g (78%) of the title ketone: IR 1678, 1640 cm^{-1}; ^{1}H NMR δ 7.6–7.3 (m, 4 H), 7.4–7.1 (m, 6 H), 5.6–5.2 (m, 1 H), 4.81 (br d, 1 H, J = 2.4 Hz), 4.67 (m, 1 H), 2.01 (m, 4 H), 1.27 (s, 6 H), 0.59 (s, 3 H); ^{13}C NMR δ 214.4, 136.6, 134.3, 133.1, 128.6, 126.8, 114.7, 42.5, 39.5, 27.8, 21.7, –5.8; MS 322 (16), 281 (12), 203 (30), 198 (15), 197 (74), 195 (12), 138 (11), 137 (100), 121 (11), 119 (11), 105 (19), 91 (12). Anal. Calcd for $C_{21}H_{26}OSi$: C, 78.18; H, 8.06. Found: C, 77.95; H, 8.17.

6-(Diphenylmethylsilyl)-4,6-dimethyl-1-hepten-5-one (2h). A mixture of 34.8 mmol of vinylmagnesium bromide and 1.89 g (6 mmol) of **1g** was heated to reflux in THF for 17 h and cooled, and then 0.98 mL of HMPA and 1.7 mL (12 mmol) of iodomethane were added. The reaction mixture was stirred at room temperature for 30 min and stirred 10 min with 80 mL of ether and 2 mL of water. The organic layer was decanted, and the solids were washed with ether. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed at reduced pressure. Silica gel chromatography gave 1.50 g (75%)

of the title ketone; IR 1678, 1640 cm^{-1}; ^1H NMR δ 7.57–7.4 (m, 4 H), 7.30–7.15 (m, 6 H), 5.17 (t, 1 H, J = 7.4 Hz), 4.84 (d, 1 H, J = 0.7 Hz), 4.68 (dd, 1 H, J = 2.71, 5.9 Hz), 1.98 (sextet, 1 H, J = 6.6 Hz), 1.51 (m, 2 H), 1.32 (s, 3 H, one of two diastereotopic methyls), 1.29 (s, 3 H, one of two diastereotopic methyls), 0.70 (d, 3 H, J = 6.6 Hz), 0.59 (s, 3 H); ^{13}C NMR δ 218.2, 134.9, 134.4, 133.4, 128.6, 126.7, 116.5, 42.8, 41.2, 37.6, 21.8, 16.4, −6.2; MS 336 (39), 321 (28), 295 (30), 217 (11), 197 (42), 175 (17), 139 (16), 138 (12), 137 (100), 121 (10), 105 (18). Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.51; H, 8.38. Found: C, 78.30; H, 8.47.

7-(Diphenylmethylsilyl)-2,4,4,7-tetramethyloct-2-en-6-one (2i). Following the procedure above 0.63 g (2 mmol) of **1h** was treated with 15.3 mL of a 0.56 M solution (8.6 mmol) of (2-methyl-1-propenyl)magnesium bromide in THF. The reaction mixture was heated to reflux for 17 h and hydrolyzed with 60 mL of moist ether. Flash chromatography of the crude reaction product gave 0.32 g (42%) of the title ketone: IR 1678 and 1650 cm^{-1}; ^1H NMR δ 7.5 (m, 4 H), 7.3 (m, 6 H), 4.95 (m, 1 H), 2.16 (s, 2 H), 1.50 (d, 3 H, J = 1.22 Hz), 1.46 (d, 3 H, J = 1.22 Hz), 1.23 (s, 6 H), 0.91 (s, 6 H), 0.57 (s, 3 H); ^{13}C NMR δ 213.3, 135.3, 134.4, 133.7, 129.4, 129.2, 127.7, 52.1, 42.3, 34.3, 28.8, 27.1, 22.1, 18.8, −5.4. Anal. Calcd for $C_{25}H_{34}OSi$; C, 79.38; H, 8.99. Found: C, 79.46; H, 9.05.

4-Methyl-4-(diphenylmethylsilyl)-1,8-nonadien-5-one (2j). In an analogous procedure to that above, 5.75 mmol of **1k** and 23 mmol of vinylmagnesium bromide gave 1.40 g (70%) of the title dienone: n^{20}_D 1.5556; IR 1672, 1635 cm^{-1}; ^1H NMR δ 7.57–7.14 (m, 10 H), 5.38–5.23 (m, 2 H), 4.86–4.58 (m, 4 H), 2.96 (dd, 1 H, J = 5.71 Hz, J = 8.1 Hz), 2.11 (d, 1 H, J = 8.13 Hz). The second diastereotopic allylic hydrogen is coincident with the following peaks: δ 1.92 (br s, 4 H), 1.21 (s, 3 H); ^{13}C NMR δ 212.5, 137.3, 135.1, 134.1, 133.6, 129.4, 117.3, 114.4, 46.2, 40.1, 39.1, 27.5, 17.3, −5.9; MS 348 (2), 199 (10), 198 (17), 197 (74), 195 (17), 169 (10), 165 (10), 137 (86), 121 (12), 119 (31), 105 (43), 93 (35), 91 (45), 79 (24), 78 (77), 77 (49), 68 (16), 67 (42), 65 (23), 56 (11), 55 (100), 54 (17), 53 (57), 51 (31). Anal. Calcd for $C_{23}H_{28}OSi$: C, 79.32; H, 8.04. Found: C, 79.17; H, 8.24.

Preparation of 10-Nonadecanone (Representative Procedure). A standard apparatus was charged with 10.5 mL (8 mmol) of a 0.76 M solution of nonylmagnesium bromide and 0.79 g (2 mmol) of **1d** in 10 mL of THF. The reaction mixture was refluxed for 60 h and cooled to 0 °C. Moist ether was added to the reaction mixture until the salts precipitated. The solvent was transferred by means of a syringe to a second flask, and the solids were washed with ether (3 × 10 mL). The solvent was removed at reduced pressure, the crude product showing a carbonyl stretch at 1690 cm^{-1} for the expected β-keto silane. This material was then stirred with 10 mL of saturated potassium fluoride in methanol for 10 h. (Alternatively the reaction mixture can be treated directly with concentrated sulfuric acid). The reaction mixture was diluted with hexane (50 mL) and washed with water (2 × 10 mL) and the aqueous layer extracted with hexane (10 mL). The solvents were removed at reduced pressure and the resulting white solid crystallized from methanol to give 0.39 g (70%) of the title ketone, mp 57–58 °C.

Preparation of 15-Methyl-16-tritriacontanone. A mixture of 20 mmol of pentadecanylmagnesium bromide and **1f** in 20 mL of THF was heated to reflux for 72 h, and then 150 mL of THF was added, the reaction mixture cooled to 0 °C, and 1 mL (7 mmol) of diisopropylamine added. The reaction mixture was stirred for 1 h at that temperature followed by the addition of iodomethane (30 mmol) and 3 mL of HMPA. Following the workup as described above, the crude β-keto silane was stirred with 40 mL of saturated potassium fluoride in methanol at reflux for 24 h. The reaction mixture was diluted with hexane (100 mL), washed with water, and dried over anhydrous magnesium sulfate. The crude material resulting from solvent removal at reduced pressure was purified by silica gel chromatography, eluting initially with hexane and then 5% ethyl acetate/hexane. The hexane fraction contained pentadecane and the polar fractions a beige solid that was recrystallized from methanol to give 1.8 g (73%) of the title ketone: mp 71–73 °C; IR (KBr pellet) 1705 cm^{-1}; ^1H NMR δ 2.3–2.2 (m, 3 H), 1.6–0.8 (m, 65 H); ^{13}C NMR δ 211.6, 42.8, 39.3, 31.9, 30.3, 29.7, 29.3, 23.9, 22.7, 14.1; MS 492 (1), 267 (100). Anal. Calcd for $C_{34}H_{68}O$: C, 82.80; H, 13.80. Found: C, 81.38; H, 13.90. This material contained about 5% pentadecane.

Preparation of 4-Methyl-1,8-nonadien-5-one. A standard apparatus of 25-mL volume was charged with 12.9 mmol of vinylmagnesium bromide in THF and 1.01 g (3 mmol) of **1k** was then added dropwise with rapid stirring. The resulting solution was heated to reflux for 23 h, cooled to room temperature, and transferred to an Erlenmeyer flask containing 100 mL of moist ether. This solution was dried with sodium sulfate and filtered and the solvent removed under reduced pressure. The crude product was treated with 20 mL of saturated potassium fluoride in methanol for 22 h at room temperature. The reaction mixture was diluted with hexane (25 mL) and washed with water, and the organic phase was dried over anhydrous magnesium sulfate. The solvent was removed by simple distillation. Flash distillation of the product gave 0.35 g (67%) of the expected ketone: n^{20}_D 1.4460; IR 1710, 1640 cm^{-1}; ^1H NMR δ 5.96–5.42 (m, 2 H), 5.05–4.8 (m, 4 H), 2.6–1.9 (m, 7 H), 1.0 (d, 3 H, J = 6.8 Hz); ^{13}C NMR δ 212.0, 137.0, 135.6, 115.0, 116.6, 45.9, 40.9, 29.3, 27.5, 15.9; MS 152 (1), 55 (100). Anal. Calcd for $C_{10}H_{16}O$; C, 78.96; H, 10.52. Found: C, 78.80; H, 10.51.

Preparation of 4,6-Dimethyl-1-hepten-5-one. A standard apparatus of 50-mL volume was charged with 26.4 mmol of vinylmagnesium bromide in 30 mL of THF, followed by the addition of 1.25 g (4 mmol) of **1g** in 6 mL of THF. The reaction mixture was heated to reflux for 17 h and cooled to room temperature, and 0.22 g of HMPA was added. This solution was stirred for 10 min, and 1.14 g (0.5 mL, 7.3 mmol) of iodomethane was added. The resulting reaction mixture was then stirred for 30 min. The organic layer obtained after a standard workup was treated with 20 mL of a saturated potassium fluoride in methanol solution. Workup as above and flash distillation gave 0.33 g (59%) of the title ketone: IR 1712, 1642 cm^{-1}; ^1H NMR δ 5.95–5.49 (m, 1 H), 5.14–4.89 (m, 2 H), 2.88–2.58 (m, 2 H), 2.57–1.88 (m, 2 H), 1.08 (d, 3 H, J = 7.0 Hz), 1.07 (d, 3 H, J = 6.8 Hz), 1.05 (d, 3 H, J = 6.8 Hz); ^{13}C NMR δ 217.3, 135.8, 116.5, 44.0, 39.6, 37.3, 18.2, 18.0, 16.4; MS 140 (8), 69 (100). Anal. Calcd for $C_9H_{16}O$; C, 77.14; H, 11.43. Found: C, 77.28; H, 11.50.

Preparation of (*Z*)-6-Heneicosen-11-one (16). A standard apparatus of 25-mL volume was charged with 11 mL (8 mmol) of 0.73 M **14** in THF and 0.86 mL (4.8 mmol) of HMPA. With rapid stirring, 0.82 g (2 mmol) of **1f** was added. The reaction mixture was stirred at reflux for 120 h and cooled to room temperature, and then 75 mL of moist ether followed by anhydrous sodium sulfate was added. The solvents were removed from the solids by decantation and removed from the reaction mixture in vacuo. This produced an oil, which showed a carbonyl stretch in the infrared at 1690 cm^{-1} for the β-keto silane. The crude β-keto silane was treated with 25 mL of saturated KF in methanol at room temperature for 12 h. This reaction mixture was diluted with hexane (50 mL), washed with water (2 × 20 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo to produce crude **16**. The pheromone was purified by silica gel chromatography, eluting with ethyl acetate/hexane (5:95). The thusly purified material showed n^{20}_D 1.4590 (lit.[27d] 1.4550) and ^1H NMR and ^{13}C NMR spectra coincident with those published.[27e,f,j] Subjection of the sample to GC–MS analysis (silica-fused 30 m × 0.3222 mm DB-1701 column) showed it to be greater than 99.9% of the desired *Z* isomer.

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Supplementary Material Available: Full listings of references for footnotes 7 and 10 and physical data for olefins and ketones prepared (8 pages). Ordering information is given on any current masthead page.