(d, J = 4.5 Hz, 2 H), 5.08 (td, J = 4.5 and 6.5 Hz, 1 H), 5.28 (dd, J = 6.5 and 1.5 Hz, 1 H), 7.64 (d, J = 2 Hz, 1 H)]. From the relative peak intensities of the vinylic proton adsorptions in ^{1}H NMR, a 1:4 molar ratio for **13b**/**15** could be deduced, thus indicating that this procedure was not of preparative value for the synthesis of **13b** and hence of **4a**.

5,6-Anhydro-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone (16d). The crude aqueous epoxide **16d**, described in the four-stage preparation of **4a** (vide supra), was—after removal of insoluble silver salts by filtration—extracted exhaustively with dichloromethane (1 × 200, 5 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo below 30 °C to give an essentially pure (^{1}H NMR) colorless oil (12.5 g, 99%), which could be distilled (bp 110 °C, 1 mm) to give analytically pure **16d** (8.3 g, 66%): $[\alpha]^{20}_D$ −143° (*c* 1.09, water); IR (neat, cm^{-1}) ν_{max} 1790–1750 (C=O), 1610 (C=C), 820 (C–O, epoxide; ^{1}H NMR ($CDCl_3$) δ 2.83 (d, J = 2.5 Hz, 1 H), 2.88 (d, J = 3.5 Hz, 1 H), 3.10 (ddd, J = 5, 3.5 and 2.5 Hz, 1 H), 4.85 (dt, J = 5 and 1.75 Hz, 1 H), 6.21 (dd, J = 5.5 and 1.75 Hz, 1 H), 7.56 (dd, J = 5.5 and 1.75 Hz, 1 H).

5(*S*)-(Hydroxymethyl)-2(5*H*)-furanone [2,3-Dideoxy-D-pent-2-enono-1,4-lactone] (1a). A suspension of D-ribono-1,4-lactone (50 g, 0.33 mol) in HBr–AcOH (33%, 250 mL, ~1.4 mol of HBr) was stirred at 30 °C for 3 h. The resulting solution was then treated dropwise with acetic anhydride (100 mL, ~10 mol) over 1 h, with the temperature kept below 30 °C. The mixture was allowed to stir at room temperature for 1 h more, when it was treated with a mixture of water (1.5 L) and dichloromethane (500 mL). The organic layer was separated after 15 min, and the aqueous phase was extracted with additional dichloromethane (3 × 250 mL). The combined extracts were washed with water (2 × 250 mL), dried ($MgSO_4$), and concentrated in vacuo to yield a mixture (93 g) (6:1) of the monobromo diacetate **17a** [^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3 H), 2.15 (s, 3 H), 4.2–4.7 (m, 4 H), 5.36 (t, J = 3.5 Hz, 1 H)] and the dibromo monoacetate **17b** [^{1}H NMR ($CDCl_3$) δ 3.72 (d, J = 6 Hz, CH_2Br]. A stirred solution of this product mixture (93 g) in propan-2-ol–water (3:1, 1 L) was treated with $NaHSO_3$ (35 g, 0.33 mol) in one portion and then portionwise with Na_2SO_3 (84 g, 0.67 mol), with the temperature prevented from exceeding 30 °C. After a period of 3 h at room temperature the solution was poured into a vigorously stirred mixture of ice-cold 2 M HCl (500 mL) and dichloromethane (750 mL). The separated aqueous phase was further extracted with dichloromethane (2 × 375 mL), and the combined extracts were washed with brine, dried ($MgSO_4$), and evaporated in vacuo. The residual oil (50 g, 96%) was shown (^{1}H NMR) to be a mixture (6:1) of butenolides **18a** [^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3 H), 4.34 (d, J = 4.5 Hz, 2 H), 6.19 (dd, J = 5.5 and 2 Hz, 1 H), 5.27 (tdd, J = 4.5, 2 and 1.5 Hz, 1 H), 7.50 (dd, J = 5.5 and 1.5 Hz, 1 H)] and **18b** [δ 3.62 (d, J = 5 Hz, CH_2Br)]. A solution of this mixture (50 g) in 1 M methanolic HCl (600 mL) was stirred at 5 °C for 18 h and evaporated in vacuo to give an oil, which was composed (TLC; CH_2Cl_2–EtOAc, 4:1) of the title furanone **1a** and the 5-bromo compound **18b**. Column chromatography (silica gel, 150 g, eluted with the same solvent mixture) gave **18b**; continued elution with EtOAc gave pure **1a** as a colorless oil, which solidified on storage at 0 °C (18.7 g, 48%). A portion of this product was distilled in vacuo, bp 140 °C (0.3 mm), which crystallized spontaneously on standing: mp 39–41 °C; $[\alpha]^{20}_D$ −140° (*c* 3.0, H_2O) [lit.[15b] mp 37–39 °C; $[\alpha]^{20}_D$ −143° (*c* 1.14, water)]; ^{1}H NMR ($CDCl_3$–CD_3OD, 3:1) δ 3.75 (dd, J = 12 and 4 Hz, 1 H), 3.85 (dd, J = 12 and 4 Hz, 1 H), 4.3 (s, 1 H), 5.15 (tdd, J = 4, 2 and 1.5 Hz, 1 H), 6.13 (dd, J = 5.5 and 2 Hz, 1 H), 7.58 (dd, J = 5.5 and 1.5 Hz, 1 H). Anal. Calcd for $C_5H_6O_3$ (MW 114.10): C, 60.06; H, 6.05. Found: C, 60.0; H, 6.2.

5(*S*)-[(Triphenylmethoxy)methyl]-2(5*H*)-furanone (1c). A stirred solution of butenolide **1a** (257 mg, 2.25 mmol) in dichloromethane-pyridine (4:1, 5 mL) was treated with triphenylmethyl chloride (700 mg, 2.50 mmol) and the mixture allowed to stir at room temperature for 4 h. The solution was diluted with ether (12.5 mL) and washed repeatedly with water and the dried ($MgSO_4$) extract concentrated in vacuo to yield a semisolid residue, which was triturated with pentane to give the title product (710 mg, 88%). Recrystallization from propan-2-ol yielded analytically pure material (400 mg, 50%): mp 152–154 °C [lit.[6a] mp 153–154 °C; lit.[15b] mp 152–154 °C; lit.[16] mp 151–153 °C[; $[\alpha]^{20}_D$ −94° (*c* 2.01, $CHCl_3$) [lit.[6a] [α] −95.9°; lit.[15b] [α] −95.1°; lit.[16] [α] −50.2° ($CHCl_3$)]; ^{1}H NMR ($CDCl_3$) δ 3.35 (d, J = 5 Hz, 2 H), 4.99 (tdd, J = 5, 2, and 1.5 Hz, 1 H), 6.07 (dd, J = 6 and 2 Hz, 1 H), 7.1–7.5 (m, 16 H). Anal. Calcd for $C_{24}H_{20}O_3$ (MW 356.42): C, 80.88; H, 5.66. Found: C, 81.0; H, 5.6.

Registry No. **1a**, 78508-96-0; **1c**, 76236-32-3; **3a**, 102335-47-7; **4a**, 102335-56-8; **7a**, 50-81-7; **7b**, 89-65-6; **8a**, 1128-23-0; **10a**, 111975-45-2; **10b**, 69617-71-6; **13a**, 111975-46-3; **13b**, 111975-50-9; **14**, 69617-82-9; **15**, 71671-99-3; **16a**, 111975-47-4; **16b**, 111975-51-0; **16c**, 111975-48-5; **16d**, 111975-52-1; **17a**, 71671-95-9; **17b**, 78139-04-5; **18a**, 85846-83-9; **18b**, 85694-09-3; **19**, 111975-49-6; D-ribono-1,4-lactone, 5336-08-3.

Methyldiphenylsilylation of Ester and Lactone Enolates[1]

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The reactions of a variety of ester and lactone enolates with methyldiphenylchlorosilane were studied. The C- versus O-silylation, leading to the α-silyl ester or lactone and silyl ketene acetal, respectively, was studied as a function of the structure of the ester or lactone and the reaction conditions. It was found that all simple acetates are C-silylated irrespective of the steric demands of the alcohol portion of the ester. Esters that are monosubstituted in the α-position are cleanly C-silylated with the notable exceptions of ethyl phenylacetate and ethyl phenoxyacetate, both of which give mixtures of C- and O-silylation. The α,α-disubstituted esters give only O-silylation, but the α,α-substituted α-silyl esters are readily prepared by the alkylation of the appropriate monosubstituted α-silylated ester. The reaction of the lithium enolate of ethyl acetate and *tert*-butyl acetate with (*S*)-(−)-1-naphthylphenylmethylchlorosilane showed the reaction to occur with inversion of configuration at silicon. Methylation of *tert*-butyl (1-naphthylphenylmethylsilyl)acetate gave a 91:9 mixture of diastereomeric α-silyl propionates, which could not be separated. It was found that only the γ-lactones gave C-silylation with δ-valerolactone and ϵ-caprolactone giving O-silylation.

The silylation of ester or lactone enolates can occur to produce the silyl ketene acetals or the α-silyl esters or lactones, all synthetically useful classes of compounds, as a result of silylation at the O- or C-terminus of the enolate

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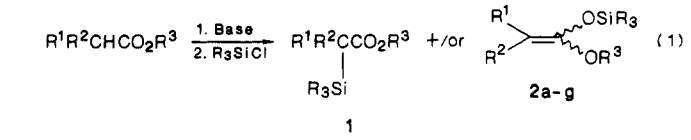
anion, respectively[4] (eq 1). Whereas examples of both O-



(1)

and C-silylation of ester or lactone enolates exist, by far the dominant pathway is that of O-silylation, owing in large part to the strength of the silicon–oxygen bond.[5] It is not surprising, therefore, that the synthetic utility of silyl ketene acetals is both well-known and widely applied.[6] Although numerous syntheses of α-silyl esters have been reported, it was not until our discovery that lithium ester enolates could be directly C-silylated with methyldiphenylchlorosilane that this class of compounds became generally available and recognized as useful synthetic reagents.[7]

Thermodynamically, one can calculate that the formation of the silyl ketene acetal would be favored by the formation of the Si–O bond (123 kcal/mol) over the α-silyl ester with the formation of the Si–C bond (73 kcal/mol).[8] On the other hand, the O-silylated isomer is disfavored by the formation of the carbon–carbon double bond (145 kcal/mol) versus the carbon–oxygen double bond (175 kcal/mol).[9] This provides a 15–28 kcal/mol advantage to the O-silylated ketene acetal structure, depending on which values one chooses to employ for the carbon–carbon and carbon–oxygen double bond energies. An argument that O-silylation is disfavored by the disruption of the resonance interaction between the carbonyl group and the ester oxygen is, at least in part, supported by the fact that ketone enolates, where this interaction is not possible, are completely O-silylated[10] and that amide enolates, where this interaction is even greater, are predominantly C-silylated.[11] Considerable evidence exists to indicate that the C-silylated isomers are thermodynamically more stable than the O-silylated counterparts, except where the α-carbon is sterically encumbered.[12] The nature of the enolate has been shown to have an effect on the O- versus C-silylation. Zinc enolates, generated in a Reformatsky approach, give C-silylation,[13] whereas lithium enolates give both O- and C-silylation[5a] and sodium enolates give only O-silylation.[14] These results are consistent with studies on the methylation and acylation of ester enolates. It has been reported that changing the solvent medium from THF to THF–HMPA leads to more C-silylation when lithium enolates are treated with trialkylchlorosilanes.[5a] This is contrary to the expectation that the effect of polar solvents would be to produce a more negative enolate anion and thereby increase reaction at the more electronegative oxygen terminus. The reaction of methyldiphenylchlorosilane with lithium ester enolates, on the other hand, gives C-silylation in THF and O-silylation in THF–HMPA.[15] Clearly, the silylation of ester and lactone enolates will depend on several factors. Since it has proven the most consistent in our hands and because the resulting C-silylated esters have been shown to be useful synthetic tools, we have chosen to employ methyldiphenylchlorosilane in the silylation of a variety of ester and lactone enolates and to study the reaction as a function of the structure of the ester and lactone and to a lesser extent as a function of the gegenion and the reaction conditions.

Results and Discussion

Spectroscopic Analysis. Because the analysis of the C- versus O-silylation of the ester and lactone enolates was best carried out via spectral methods, we first discuss the spectral characteristics of the α-methyldiphenylsilyl esters and the methyldiphenylsilyl ketene acetals. It was found that the course of the reaction could be followed qualitatively by infrared spectroscopy and quantitatively by NMR spectroscopy. The infrared spectra of the α-silyl esters in general show a carbonyl stretch at ca. 1715 cm^{-1}, some 15–20 cm^{-1} less than the parent esters. The α-(methyldiphenylsilyl)-γ-lactones, the only ones that show C-silylation, show a carbonyl stretch near 1750 cm^{-1}, about the same as the parent γ-lactones. The silyl ketene acetals show a double bond stretch near 1665 cm^{-1} except for those of ethyl and methyl isobutyrate, which show this stretch at 1715 and 1710 cm^{-1}, respectively.[16] Carbon-13 NMR spectroscopy clearly distinguishes between the C- and O-silylated products with the α-silyl esters showing the expected resonance at about 170–175 ppm for the carbonyl carbon and the silyl ketene acetal resonances near 148 and 90–102 ppm for the β- and α-vinyl carbons, respectively. In addition, the α-carbon of the α-silyl esters resonates at ca. 30 ppm as predicted. Silicon-29 spectroscopy in conjunction with the other spectroscopic evidence available proved to be useful with the silicon of the α-silyl esters resonating in general between −4 and −6 ppm with respect to tetramethylsilane, and the silicon of the silyl ketene acetals, resonating at slightly higher field, falling between −2 and −3 ppm. The proton NMR spectra shows multi-

(1) The chemistry of α-silyl carbonyl compounds, part 17.
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Table I. Yields and Key Spectral Data for the α-Silyl Esters and Lactones

entry	R_3Si	R^1	R^2	R^3	compd	% yield	C=O stretch	SiC*H*	$SiCH_3$	$SiCH_3$	SiCH	C=O	Si
1	Ph_2MeSi	H	H	Et	**3a**	90	1722	2.4	0.68	−3.9	24.9	171.9	
2	Ph_2MeSi	H	H	i-Pr	**3b**	86	1705	2.38	0.68	−3.9	25.2	171.6	
3	Ph_2MeSi	H	H	*t*-Bu	**3c**	91	1710	2.34	0.69	−4.0	25.9	171.0	
4	Ph_2MeSi	H	H	C_3H_5	**3d**	71	1720	2.44	0.69	−3.9	24.9	171.8	
5	Ph_2MeSi	H	H	2,6-di-*t*-BuC_6H_3	**3e**	11	1730	2.74	0.81	−3.9	25.8	172.1	
6	1-NpPhMeSi	H	H	Et	**11**	84	1715	2.57	0.76	−2.2	26.7	172.0	
7	1-NpPhMeSi	H	H	*t*-Bu	**12**	58	1740	2.29	0.77	−2.2	26.7	171.5	
8	Ph_2MeSi	H	Me	Et	**4a**	93	1720	2.58	0.65	−5.7	28.8	175.7	−4.1
9	Ph_2MeSi	H	Me	*i*-Pr	**4b**	79	1710	2.61	0.66	−5.5	28.9		−5.6
10	Ph_2MeSi	H	Me	C_3H_5	**4c**	65	1725	2.69	0.65	−5.6	28.9		−4.9
11	Ph_2MeSi	H	Me	*t*-Bu	**4d**	93	1709	2.57	0.66	−5.5	29.5	174.9	−5.3
12	1-NpPhMeSi	H	Me	*t*-Bu	**13**	96	1730	2.63	0.72, 0.71	−3.4, −3.6	29.9, 29.8	175.2, 174.9	
13	Ph_2MeSi	H	Et	Et	**4e**	76	1710	2.5	0.65	−5.5	28.5	174.6	
14	Ph_2MeSi	H	Et	*t*-Bu	**4f**	93	1709	2.65	0.61	−5.5	28.9	173.9	
15	Ph_2MeSi	H	*n*-Pr	Et	**4g**	84	1710	2.54	0.66	−5.5	29.5	175.0	
16	Ph_2MeSi	H	*n*-C8H17	Et	**4h**	95	1710	2.56	0.65	−5.5	29.2	175.1	
17	Ph_2MeSi	H	CH_2=$CH(CH_2)_7$	Et	**4i**	90	1715	2.48	0.65	−5.5	29.1	175.0	
18	Ph_2MeSi	H	*n*-$C_{16}H_{33}$	Et	**4j**	91	1715	2.37	0.60	−5.7	29.4	174.7	−6.2
19	Ph_2MeSi	H	C3H5	Et	**4k**	83	1710	2.2	0.68	−5.5	31.7	173.4	
20	Ph_2MeSi	H	$CH_3C(O)CH_2$[a]	Et	**4l**	82	1715	2.8	0.65	−5.3	30.9	175.2	
21	Ph_2MeSi	H	$CH_3C(O)CH_2CH$[a]	Et	**4m**	78	1715	2.8	0.65	−5.7	34.1	174.6	
22	Ph_2MeSi	Me	CH_2=CH	Et	**4n**	60	1720	3.5	0.60	−5.5	43.6	172.4	
23	Ph_2MeSi	Me	Me	Et	**7a**	87	1708		0.68	−5.3	32.6	178.0	−3.8
24	Ph_2MeSi	Me	*n*-Pr	Et	**7b**		1710		0.68	−5.2	43.6	174.7	
25	Ph_2MeSi	Me	C_3H_5	Et	**7c**	79	1710		0.68	−5.2	37.0	176.5	
26	Ph_2MeSi	Me	*n*-C_8H_{17}	Et	**7d**	95	1710		0.68	−5.3	31.7	177.0	
27	Ph_2MeSi	Me	CH_2=$CH(CH_2)_7$	Et	**7e**	65	1710		0.65	−5.2	36.3	175.0	
28	Ph_2MeSi	Me	CH_2=CH	Et	**7f**	83	1710		0.73	−5.2	43.6	174.7	
29	Ph_2MeSi		$(CH_2)_2$	Et	**8a**	83	1730		0.67	−3.3	18.1	173.2	−3.4
30	Ph_2MeSi		$(CH_2)_3$	Et	**8b**	84	1710		0.73	−6.0	37.9	177.3	−6.2
31	Ph_2MeSi		see **10a**		**10a**	95	1745	2.8	0.66	−4.5	28.7	179.1	
32	Ph_2MeSi		see **10b**		**10b**	96	1745	2.8	0.73	−4.5, −4.9	30.2, 30.5	178.3	
33	Ph_2MeSi		see **10c**		**10c**	75	1745	2.4	0.72	−3.9	30.3	177.1	

[a] As ethylene ketal.

Table II. Yields and Key Spectral Data for the Silyl Ketene Acetals

entry	ketene acetal	% yield	C=C stretch	C=C*H*	$SiCH_3$	$SiCH_3$	C=COSi	*C*=C	Si
1	**6**	89	1715		0.72	−2.9	148.3	92.3	−2.99
2	**2a**	81	1680	2.25	0.32	−2.3	120.07	83.3	1.09
3	**2b**	85	1710		0.72	−2.9	149.7	91.3	−2.88
4	**2c**	87[a]	1660	*b*	*b*	−3.1	143.96	95.31	−3.26
5	**2d**	90[a]	1650	4.55, 4.43	*b*	−0.7	156.4	123.4	
6	**2e**	82[a]	1665		0.73	−3.1	159.4	121.4	−3.19
7	**9a**	85	1710	*b*	*b*	−2.7	146.1	102.3	−3.3
8	**9b**	81	1695	*b*	*b*	−2.95	145.85	100.77	−2.74

[a] The enol silyl ether is mixed with the corresponding α-silyl ester. [b] No hydrogen spectrum was taken.

plets at about 2.2–2.6 ppm for the α-protons of the α-silyl esters and near 4.2 ppm for those silyl ketene acetals bearing a vinyl hydrogen. The chemical shifts of the silicon methyls remain rather constant and are of no help in assigning the structures. The key spectral properties of the compounds produced in this study are shown in Tables I and II.

Methyldiphenylsilylation of Acetates. In our first set of experiments, we investigated the silylation of a series of acetates as a function of the steric requirements of the alcohol portion of the ester. In all cases studied, the enolates of these acetates were clearly C-silylated with methyldiphenylchlorosilane to give the α-silyl ester in good to excellent yield when the lithium enolate was generated in THF solvent (eq 2). The use of a THF–HMPA solvent

$$CH_3CO_2R^3 \xrightarrow[2.\ Ph_2MeSiCl]{1.\ LDA/THF} Ph_2MeSiCH_2CO_2R^3 \quad (2)$$

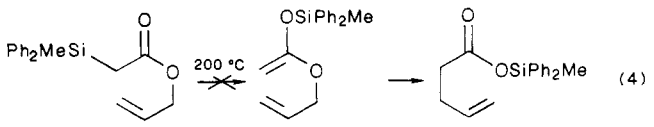
3a-f

mixture, however, gave a mixture of C- and O-methyldiphenylsilylation under otherwise identical conditions. Subjection of ethyl (methyldiphenylsilyl)acetate to the reaction conditions with the THF–HMPA solvent system showed no isomerization to the O-silylated material. The possibility of the reaction being the result of a greater steric effect imparted by the methyldiphenylsilyl group is inconsistent with the O-silylation observed with *tert*-butyldimethylchlorosilane.[5a] Attempts to silylate ethyl lithioacetate with *tert*-butyldiphenylchlorosilane in THF gave no product. Further evidence for the negative effect of greater steric hindrance is seen by the 11% yield of α-silyl ester **3e**. One further manifestation of possible steric influence on the reaction is the C-trimethylsilylation of (−)-menthyl acetate.[7c] It proved impossible to thermally isomerize the α-methyldiphenylsilyl acetates to their isomeric silyl ketene acetals. It was possible, however, to thermally isomerize the methyldiphenylsilyl ketene acetal of ethyl acetate to the C-silylated isomer by heating to ca. 200 °C under nitrogen or by Kugelrohr distillation (eq 3).

$$CH_3CO_2R^3 \xrightarrow[2.\ Ph_2MeSiCl]{1.\ LDA/THF\text{-}HMPA} CH_2{=}C(OSiR_3)(OR^3) \xrightarrow{200\ ^\circ C} Ph_2MeSiCH_2CO_2R^3 \quad (3)$$

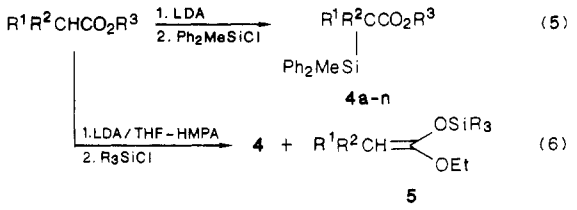
Further evidence for a lack of isomerization from the C- to the O-silylated material is seen in that the attempted thermolysis at 200 °C of the α-methyldiphenylsilyl ester of allyl acetate, which would have been expected to provide the methyldiphenylsilyl ester of 4-pentenoic acid, also showed no reaction indicating that the silyl ketene acetal

is not even present in small amounts in equilibrium with the C-silylated isomer under these conditions (eq 4).



(4)

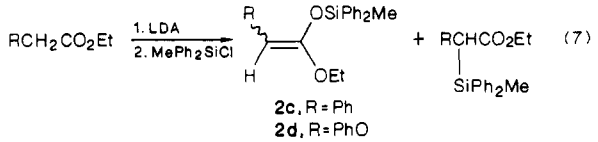
Methyldiphenylsilylation of Monosubstituted Acetates. In the course of our studies on the synthetic applications of α-silyl esters, we have C-silylated a variety of monosubstituted ethyl acetates via the reaction of their lithium enolates with methyldiphenylchlorosilane in THF solvent. In the straight-chain alkyl series, ranging from ethyl propionate to ethyl stearate, no evidence was found for O-methyldiphenylsilylation when methyldiphenylchlorosilane was reacted with the lithium enolate of the ester in the THF solvent. In this study, we looked at the methyldiphenylsilylation of a series of propionates as a function of the alcohol portion of the ester. Only C-silylation was observed in all cases (eq 5). Thus, increased steric requirements on the alcohol portion of the propionates has no effect on the regioselectivity of the silylation. On the other hand, employing THF–HMPA as solvent or dimethylphenylchlorosilane as the silylating agent produces a mixture of C- and O-silylated products from ethyl propionate (eq 6).



(5)

(6)

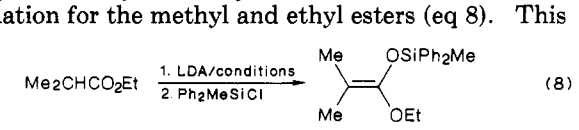
Two other monosubstituted acetates, ethyl phenylacetate and ethyl phenoxyacetate, were studied. Ethyl phenylacetate, under the conditions of deprotonation with LDA in THF, gives O-silylation (**2c**), but, somewhat surprisingly, a 63:37 ratio of C- to O-silylation in THF–HMPA and a 53:47 C- to O-silylation ratio with dimethylphenylchlorosilane in THF (eq 7). The increased amount



(7)

of O-silylation in this system can be attributed to the increased stability of the styrene-like double bond of the resulting silyl ketene acetal. Treatment of **4a** with a THF–HMPA solution of diisopropylamine showed no isomerization to the silyl ketene acetal **5** (R^2 = Me), indicating that the products were formed under kinetic control. Interestingly, the methyldiphenylsilylation of the lithium enolate of ethyl phenoxyacetate gives a 60:40 mixture of C- and O-silylation (**2g**) in THF or THF–HMPA.

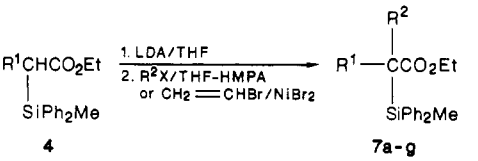
Methyldiphenylsilylation of Isobutyrate Esters. We next turned our attention to the methyldiphenylsilylation of the lithium enolates of the isobutyrate esters in order to ascertain the effect of two α-methyl groups on the regioselectivity of the silylation. This resulted in clean O-silylation for the methyl and ethyl esters (eq 8). This



(8)

could be due to the steric effect of the two methyl groups or to the increased stability of the carbon–carbon double bond of the silyl ketene acetal. Lewis acid catalyzed rearrangement of the substituted silyl ketene acetals to the α-silyl esters does not occur, indicating that the silyl ketene acetal is the thermodynamically more stable isomer in these cases.[18] In view of the clean O-silylation in these systems, we undertook a short study of the effect of the reaction conditions in the hope of finding a convenient route to these more highly substituted α-silyl esters. Changing the cation from lithium to bromomagnesium or the even more covalent chlorozinc does not lead to any C-silylation even though these cations would be expected to give the best chance for C-silylation. Increasing the steric bulk of the alcohol portion of the ester still leads to O-silylation with the lithium enolate.

It is possible to prepare α,α-disubstituted α-silyl esters via alkylation of the α-silyl esters (vida infra).[19] This was used to prepare ethyl 2-methyl-2-(methyldiphenylsilyl)-propionate in 75% yield (eq 9). This compound can be



(9)

purified by column chromatography and reacts with Grignard reagents. However, when it was subjected to the reaction conditions employed for the preparation of α-silyl esters **3** and **4**, no isomerization occurred, eliminating the possibility that the observed silyl ketene acetal was formed from an initially produced C-silylated isomer. On the basis of these results, the silylation of other α,α-disubstituted esters was not attempted. These α,α-disubstituted α-silyl esters are, however, available via the alkylation of monoalkylated α-silyl esters.

Methyldiphenylsilylation of Ethyl Cycloalkanecarboxylates. It was felt that even though the isobutyrates do not C-silylate, the cycloalkane carboxylate esters merited study. Ainsworth and co-workers[20] have shown that trimethylsilylation of the lithium enolates of ethyl cyclopropanecarboxylate and ethyl cyclobutanecarboxylate give a mixture of C- and O-silylated products. The increased formation of C-silylated products in these systems can be attributed to the lower stability of the exocyclic double bond in the silyl ketene acetals of these esters. The results of methyldiphenylsilylation of the lithium enolates of the ethyl esters of the three-through six-carbon cyclic carboxylic acids are given in Table I (entries 29 and 30) and Table II (entries 6 and 7). Consistent with an assumption that the C- versus O-silylation can depend on the stability of the carbon–carbon double bond, it was found that ethyl cyclopropane- and ethyl cyclobutanecarboxylates are C-methyldiphenylsilylated in good yield, although the reaction is cleaner at −100 °C than at −78 °C, whereas with the larger ring esters, where the exocyclic double bond does not suffer from lower stability, the silyl ketene acetals are isolated (eq 10).

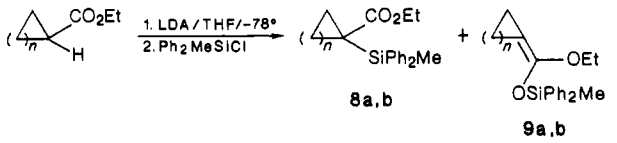
Methyldiphenylsilylation of Other Esters. On the basis of our success in converting esters to ketones via their α-silyl esters,[21] we felt that the silylation of diethyl suc-

(18) (a) Ireland, R. E.; Muller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (b) Katzenellenbogen, J. A.; Christy, K. J. *J. Org. Chem.* **1974**, *39*, 3315.

(19) Lutšenko, I. F.; Baukov, Yu. I.; Bulachenko, G. S.; Khasapov, B. N. *J. Organomet. Chem.* **1966**, *5*, 20.

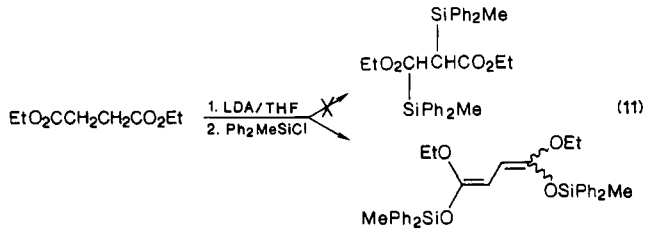
(20) Helmchen, G.; Schmierer, R. *Tetrahedron Lett.* **1983**, *24*, 1235.

(21) Larson, G. L.; Hernandez, D.; Montes de Lopez-Cepero, I.; Torres, L. E. *J. Org. Chem.* **1985**, *50*, 5260.



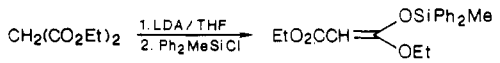
(10)

cinate, which could be a precursor to symmetrical 1,4-diketones upon treatment with a Grignard reagent followed by desilylation, was worthy of study. Unfortunately, the methyldiphenylsilylation of the dilithio enolate of diethyl succinate gives the bis-*O*-silylated material (eq 11). Ap-



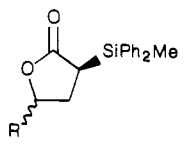
(11)

parently, the possibility of forming a conjugated diene favors O-silylation in this system. Deprotonation of ethyl crotonate with LDA in THF and treatment of the lithium enolate with methyldiphenylchlorosilane gives the O-silylated isomer. It is possible, however, to vinylate ethyl (trimethylsilyl)acetate[22] or ethyl (methyldiphenylsilyl)-acetate,[23] and the resulting α-silyl esters are stable. Deprotonation–methyldiphenylsilylation of diethyl malonate, not surprisingly, produces the O-silylated isomer with the double bond being stabilized via conjugation to the carbonyl (eq 12).

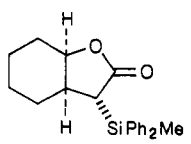


(12)

Methyldiphenylsilylation of Lactones. The methyldiphenylsilylation of the lithium enolates of γ-butyrolactone and γ-valerolactone gives the corresponding α-silyl-γ-lactone in excellent yield without any evidence for the O-silylated isomers. This C-silylation of γ-lactones is carried over to the fused cis lactone of 2-hydroxycyclohexaneacetic acid. In this system, the enolate is silylated from the β face of the molecule.[21] Contrary to the excellent results obtained with the γ-lactones, all attempts to C-methyldiphenylsilylate δ-valerolactone and ϵ-caprolactone failed, with only the O-silylated product being formed under all conditions. This could be attributed to the greater stability of the endocyclic double bonds in these ring systems as opposed to that of the five-membered ring.



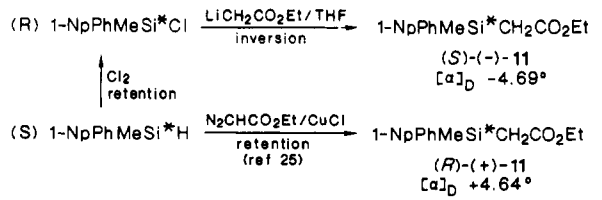
10a, R=H
10b, R=Me



10c

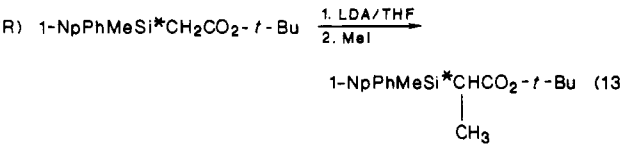
Stereochemistry at Silicon. Although we felt that the reaction of the lithium ester enolate on a chlorosilane would occur with inversion of configuration at silicon, other work in our laboratories involving asymmetric reactions of carbofunctional organosilanes as a single antipode at silicon[24] made it imperative that we determine both the stereochemistry and the stereospecificity of the reaction.

Scheme I



Thus, (*R*)-(−)-1-naphthylphenylmethylchlorosilane was reacted with ethyl lithioacetate in THF to give an 83% yield of (*S*)-(−)-**11**, which showed an absolute rotation of −4.69°. Brook and co-workers[25] have reported the preparation of (*S*)-(+)-**11** via the reaction of ethyl diazoacetate with (*R*)-(+)-1-naphthylphenylmethylsilane. Their material showed a specific rotation of +4.64°. These results are shown in Scheme I. In a similar manner, (*S*)-(−)-*tert*-butyl 2-(1-naphthylphenylmethylsilyl)acetate was formed from treatment of the optically active chlorosilane with *tert*-butyl lithioacetate.

Alkylation of α-Silyl Esters. The alkylation of α-trimethylsilyl esters has been reported.[20] We have found that the lithium enolates of the α-methyldiphenylsilyl esters are readily alkylated in the absence, or better, presence of HMPA as cosolvent (eq 13). This not only



(13)

13, 9:1 mixture of inseparable diastereomers

provides an alternate route to monoalkylated α-methyldiphenylsilyl esters but more importantly provides a route to α,α-disubstituted α-methyldiphenylsilyl esters, which are not available by direct silylation of the ester enolate. As can be seen from entries 22–28 in Table I, the alkylation proceeds as well with a long-chain alkyl bromide as it does with iodomethane.

Of particular interest is the methylation of (−)-*tert*-butyl (1-naphthylphenylmethylsilyl)acetate **12**, which provided a mixture of diastereomeric α-silylpropionates **13** in a 90:10 ratio (80% ee) as determined by ^{1}H NMR (eq 13). To our knowledge, this is the best asymmetric induction yet reported for the 1-naphthylphenylmethylsilyl group.[24] Although this material is a white solid as the mixture, all attempts to completely separate the diastereomers were unsuccessful.

Experimental Section

General Considerations. All reactions were carried out in a flame-dried, round-bottomed flask equipped with magnetic stirrer and a no-air stopper under an atmosphere of predried nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded on a JEOL FX90Q spectrophotometer and are reported as ppm with respect to internal tetramethylsilane or chloroform-*d*. GC–mass spectral analyses were performed on a Hewlett-Packard 5995A spectrometer and are reported as *m/e* (relative abundance). All solvents were distilled from sodium benzophenone ketyl (ether, THF) or calcium hydride prior to use. Some of the starting esters were prepared by standard routes whereas others were purchased and distilled prior to use. Room temperature is ca. 30 °C.

Methyldiphenylsilylation of Ester Enolates. General Procedure. A standard apparatus as described above was charged with 25 mL of THF and 2.24 mL (16 mmol) of diisopropylamine,

(22) (a) Albaugh-Robertson, P.; Katzenellenbogen, J. A. *J. Org. Chem.* **1983**, *48*, 5228. (b) Albaugh-Robertson, P.; Katzenellenbogen, J. A. *Tetrahedron Lett.* **1982**, *23*, 723.
(23) Santiago, A.; Berrios, R., unpublished work.
(24) Larson, G. L.; Torres, E. *J. Organomet. Chem.* **1985**, *293*, 19.
(25) Brook, A. G.; Duff, J. H.; Anderson, D. G. *J. Am. Chem. Soc.* **1970**, *92*, 7576.

and the apparatus was cooled to −78 °C with a dry ice–acetone bath. To this was added 10.6 mL (15 mmol) of *n*-butyllithium in hexane, and the reaction mixture was allowed to reach room temperature where it was stirred for 15 min. The LDA solution was then cooled again to −78 °C, and 15 mmol of the ester in 5 mL of THF was added via syringe. The enolate was allowed to form at −78 °C for 30 min, after which time 3.09 g (15 mmol) of methyldiphenylchlorosilane in 5 mL of THF was added, and the reaction mixture was stirred for 3 h at −78 °C and from 4 to 16 h at room temperature. In those cases where C-silylation occurred, the reaction mixture was diluted in cold hexane and washed with cold water (3 × 25 mL), and the organic layer was dried over anhydrous sodium sulfate. In those cases where O-silylation was observed in whole or in part, an anhydrous workup procedure, which consisted of diluting the reaction mixture in cold hexane, filtering the precipitated salts, and concentrating the organic solution, was followed. The anhydrous procedure was employed on all new reactions with the aqueous workup being used only on repeat reactions where the C-silylated isomers were known to be the products. The products were purified by silica gel chromatography, flash chromatography, or Kugelrohr distillation.

Ethyl 2-(Methyldiphenylsilyl)cyclopropanecarboxylate (8a). Following the general procedure for the C-silylation of ester enolates with the exception of lower temperature as noted, 1.14 g (10 mmol) of ethyl cyclopropanecarboxylate in 10 mL of THF was added dropwise to 11 mmol of LDA in 20 mL of THF at −100 °C. This solution was stirred at −100 °C for 65 min, and the resulting lithium enolate was quenched by the addition of 2.09 g (9 mmol) of methyldiphenylchlorosilane in 10 mL of THF. The reaction mixture was then allowed to slowly warm to room temperature where it was stirred overnight. Flash chromatography of the crude reaction product eluting with ethyl acetate–hexane (3:97 v/v) gave 1.6 g (58%) of the title ester: IR 1710; ^{1}H NMR δ 7.38 (m, 10 H), 3.96 (q, 2 H, J = 7.3 Hz), 1.28 (dd, 2 H, J = 2.7, 3.9 Hz), 0.94 (t, 3 H, J = 7.1 Hz), 0.74 (dd, 2 H, J = 6.7, 3.1 Hz), 0.67 (s, 3 H); ^{13}C NMR δ 175.7, 135.8, 134.9, 127.6, 129.2, 60.4, 13.8, 12.4, 9.3, −4.2; MS, m/e 310 (1), 233 (100). Anal. Calcd for $C_{19}H_{22}O_2Si$: C, 73.50; H, 7.14. Found: C, 73.41; H, 7.17.

Ethyl 1-(Methyldiphenylsilyl)cyclobutanecarboxylate (8b). Following the procedure above employing 2.6 g (20 mmol) of ethyl cyclobutanecarboxylate, 23 mmol of LDA, and 4.7 g (20 mmol) of methyldiphenylchlorosilane provided 5.0 g (77%) of the title ester: IR 1710; ^{1}H NMR δ 7.99–7.19 (m, 10 H), 3.99 (q, 2 H, J = 7.3 Hz), 2.35 (m, 6 H), 1.02 (t, 3 H, J = 7.1 Hz), 0.73 (s, 3 H); ^{13}C NMR δ 177.7, 135.1, 134.6, 129.4, 127.5, 59.8, 38.2, 28.7, 17.9, 13.9, −5.9; MS, m/e 324 (59), 197 (100). Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.07; H, 7.40. Found: C, 73.95; H, 7.50.

(*R*)-(−)-Ethyl 2-(1-Naphthylphenylmethylsilyl)acetate (11). Via the general procedure for the C-silylation of lithium ester enolates, 0.63 mL (7 mmol) of ethyl acetate was treated with 6 mmol of LDA in THF at −78 °C, and the resulting enolate was treated with 1.70 g (6 mmol) of (*S*)-(−)-1-naphthylphenylmethylchlorosilane. The crude reaction product was subjected to Kugelrohr distillation at 200 °C (0.15 mm) to give 1.67 g (83.5%) of the title ester: n^{21}_D 1.6050 [lit.[25] for *S*(+) enantiomer n^{20}_D 1.6051; $[\alpha]^{24}_D$ −4.69° [lit.[24] for enantiomer +4.64°]; IR 1715; ^{1}H NMR δ 8.00–7.15 (m, 12 H), 3.89 (q, 2 H, J = 7 Hz), 2.57 (s, 2 H), 0.91 (t, 3 H, J = 7 Hz), 0.82 (s, 3 H); ^{13}C NMR δ 172.0, 136.9, 136.2, 135.3, 134.5, 133.4, 132.9, 130.7, 129.5, 128.9, 128.4, 127.9, 125.8, 125.4, 59.9, 26.7, 13.9, −2.2; MS, m/e 335 (6), 277 (100). Anal. Calcd for $C_{21}H_{22}O_2Si$: C, 75.41; H, 9.63. Found: C, 75.13; H, 9.28.

(*R*)-(−)-*tert*-Butyl 2-(1-Naphthylphenylmethylsilyl)-acetate (12). Via the procedure above employing 6.74 mL (5.81 g, 50 mmol) of *tert*-butyl acetate and 14.15 g (50 mmol) of (*S*)-(−)-1-naphthylphenylmethylchlorosilane, silica gel chromatography of the crude reaction product eluting with ethyl acetate–hexane (2:98 v/v) provided 10.5 g (57.9%) of the title ester: mp 70–71 °C; $[\alpha]^{24}_D$ −0.85° (*c* 17.73, cyclohexane); IR 1740; ^{1}H NMR δ 7.64–6.75 (m, 12 H), 2.29 (s, 2 H), 1.03 (s, 9 H), 0.77 (s, 3 H); ^{13}C NMR δ 171.5, 136.9, 136.2, 135.3, 134.5, 133.4, 132.9, 130.7, 129.5, 128.9, 128.4, 127.9, 125.8, 125.4, 125.0, 79.7, 27.8, 26.7, −2.2; MS, m/e 363 (5). Anal. Calcd for $C_{23}H_{26}O_2Si$: C, 76.20; H, 7.23. Found: C, 76.06; H, 7.17.

Alkylation of α-Silyl Esters. General Procedure. To a prepared solution of 15 mmol of LDA in 25 mL of THF–hexane was added 10 mmol of the α-silyl ester in 10 mL of THF at −78 °C over a 15-min period. The resulting reaction mixture was stirred for 30 min at that temperature and then 10 mmol of the alkylating agent in THF or THF–HMPA was added, and the reaction mixture was allowed to warm to room temperature. The solution was washed with saturated sodium thiosulfate (2 × 25 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. This was then filtered, the solvent was removed at reduced pressure, and the crude reaction product was purified by silica gel chromatography eluting with hexane or ethyl acetate–hexane.

***tert*-Butyl 2-(1-Naphthylphenylmethylsilyl)propionate (13).** Via the general alkylation procedure above, 1 g (2.76 mmol) of **12** was treated sequentially with 4.83 mmol of LDA and 0.31 mL (0.71 g, 5 mmol) of iodomethane. The crude product was purified by silica gel chromatography eluting with ethyl acetate–hexane (2:98 v/v) to provide 1.0 g (96.1%) of the title ester as a 9:1 mixture of diastereomers as ascertained by ^{1}H NMR analysis and analytical HPLC (silica gel column, ethyl acetate–hexane). Attempted separation by crystallization gave a 2:1 mixture, which defied further separation: IR 1735; ^{1}H NMR (minor diastereomer) δ 7.60–6.83 (m, 12 H), 2.58 (q, 1 H, J = 7.5 Hz), 1.19 (d, 3 H, J = 7.5 Hz), 0.86 (s, 9 H), 0.62 (s, 3 H), (major diastereomer) δ 7.60–6.83 (m, 12 H), 2.63 (q, 1 H, J = 7.5 Hz), 1.05 (d, 3 H, J = 7.5 Hz), 1.02 (s, 9 H), 0.61 (s, 3 H); ^{13}C NMR (mixture of diastereomers) δ 175.2, 174.9, 137.1, 135.8, 135.7, 135.6, 135.5, 135.0, 134.8, 133.5, 133.2, 133.0, 130.5, 129.4, 129.0, 128.5, 127.8, 125.7, 125.4, 125.0, 79.8, 79.6, 29.9, 29.8, 27.9, 27.7, 12.4, 12.3, −3.4, −3.6; MS, m/e 376 (3), 57 (100). Anal. Calcd for $C_{24}H_{28}O_2Si$: C, 76.53; H, 7.50. Found: C, 76.80; H, 7.80.

Attempted Thermal Rearrangement of α-Silyl Esters. A heavy-walled NMR tube was dried in an oven at 120 °C for a minimum of 4 h, flushed with nitrogen, and charged with 500 mg of the ester. The tube was then cooled to −78 °C under a nitrogen atmosphere and flame sealed. The neat ester was then heated in an oil bath at temperatures ranging from 100 to 300 °C with no observable change in the ^{1}H NMR spectrum. These attempted thermolyses were carried out on esters **3a** and **3d**.

Preparation of 1-(Dimethylphenylsiloxy)-1-ethoxypropene (2a). Via the general procedure, 1.02 g (10 mmol) of ethyl propionate in 10 mL of THF was reacted with 11.5 mmol of LDA, and the enolate was quenched by the addition of 1.9 mL (11.5 mmol) of dimethylphenylchlorosilane. The crude product was purified by Kugelrohr distillation, affording 1.90 g (81%) of the title compound: bp 97–100 °C (0.6 mm); IR 1680 cm^{-1}; ^{1}H NMR δ 7.59–7.19 (m, 5 H), 4.08 (q, 1 H, J = 7.08 Hz), 2.25 (q, 2 H, J = 7.8 Hz), 1.28 (d, 3 H, J = 7.0 Hz), 1.09 (t, 3 H, J = 7.8 Hz), 0.32 (s, 6 H); ^{13}C NMR δ 139.08, 132.37, 128.68, 127.17, 120.72, 83.34, 59.39, 26.89, 13.67, 8.53, −2.25; ^{29}Si NMR δ +1.09.

Preparation of 1-(Methyldiphenylsiloxy)-1-ethoxy-2-methylpropene (6). Via the general procedure, 1.16 g (10 mmol) of ethyl isobutyrate in 10 mL of THF was reacted with 11.5 mmol of LDA, and the enolate was quenched with 2.16 mL (10 mmol) of methyldiphenylchlorosilane. Kugelrohr distillation of the crude product afforded 2.78 g (89%) of the title compound: bp 135–140 °C (0.5 mm); IR 1715 cm^{-1}; ^{1}H NMR δ 7.69–7.26 (m, 10 H), 4.04 (q, 2 H, J = 7.0 Hz), 1.53 and 1.58 (s, 6 H), 1.07 (t, 3 H, J = 7.0 Hz), 0.72 (s, 3 H); ^{13}C NMR δ 148.29, 137.46, 135.62, 129.77, 127.65, 92.27, 65.08, 16.92, 16.38, −2.90; ^{29}Si NMR δ −2.99. Similar results were obtained when HMPA (0.3 mL) was added to the reaction mixture.

Preparation of 1-(Methyldiphenylsiloxy)-1-methoxy-2-methylpropene (2b). Via the general procedure, 1.02 g (10 mmol) of methyl isobutyrate in 5 mL of THF was reacted with 11.5 mmol of LDA, and the enolate was quenched with 2.3 mL (11.5 mmol) of methyldiphenylchlorosilane. Kugelrohr distillation of the crude product afforded 2.23 g (85%) of the title compound: bp 130–132 °C (0.6 mm); IR 1710 cm^{-1}; ^{1}H NMR δ 7.62–7.36 (m, 10 H), 3.30 (s, 3 H), 1.55 (s, 6 H), 0.72 (s, 3 H); ^{13}C NMR δ 149.72, 135.45, 134.15, 129.77, 127.60, 91.30, 57.06, 16.81, 16.07, −2.90; ^{29}Si NMR δ −2.88; MS, m/e 298 (17), 197(100).

Reaction of Methyldiphenylchlorosilane with the Magnesium Enolate of Ethyl Isobutyrate. Preparation of 1-(Methyldiphenylsiloxy)-1-methoxy-2-methylpropene. Via the general procedure, 1.02 g (10 mmol) of methyl isobutyrate in 5 mL of THF was reacted with 11.5 mmol of LDA, and then 12 mmol of magnesium bromide was added. The magnesium

enolate that formed was quenched with 2.3 mL (11.5 mmol) of methyldiphenylchlorosilane. The crude product (80%) was analyzed without further purification. The ^{13}C NMR spectrum showed the presence of the title compound, starting material, and diphenylmethylsilanol: IR 1750, 1715 cm^{-1}; ^{13}C NMR (methyl isobutyrate) δ 177.28, 51.31, 33.76, 18.86, (silyl ketene acetal) δ 149.48, 91.25, 57.10, 16.85, 16.07, -2.86, (methyldiphenylsilanol) δ 137.48, 134.23, 133.90, 129.48, 127.59, -0.64.

Reaction of Methyldiphenylchlorosilane with the Zinc Enolate of Methyl Isobutyrate. Preparation of 1-(Methyldiphenylsiloxy)-1-methoxy-2-methylpropene. Via the general procedure, 0.57 mL (5 mmol) of methyl isobutyrate in 3 mL of THF was reacted with 6.5 mmol of LDA. The enolate was reacted with 0.89 g (6.5 mmol) of zinc chloride followed by quenching with 1.5 mL (6.5 mmol) of methyldiphenylchlorosilane. The crude material (85%) was analyzed without further purification: IR 1715 cm^{-1}; ^{13}C NMR δ 149.72, 135.44, 134.20, 129.77, 127.68, 91.57, 57.28, 16.87, 16.12, -3.6; ^{29}Si NMR δ -2.93 (silyl ketene acetal), -9.74 (silanol).

Reaction of Methyldiphenylchlorosilane with the Lithium Enolate of Methyl Isobutyrate Using HMPA as Cosolvent. Preparation of 1-(Methyldiphenylsiloxy)-1-methoxy-2-methylpropene. Via the general procedure, 1.02 g (10 mmol) of methyl isobutyrate in 5 mL of THF was reacted with 11.5 mmol of LDA, and the enolate was quenched with 2.16 mL (11.5 mmol) of diphenylmethylchlorosilane in 0.3 mL of HMPA. Analysis of the crude product (2.18 g, 73%) by ^{29}Si NMR showed only the silyl ketene acetal resonance at -2.90 ppm.

Reaction of Methyldiphenylchlorosilane with the Lithium Enolate of Ethyl Phenylacetate Using HMPA as Cosolvent. Attempted Preparation of Ethyl (Methyldiphenylsilyl)phenylacetate (2c). Via the general procedure, 1.64 g (10 mmol) of ethyl phenylacetate in 5 mL of THF was reacted with 11.5 mmol of LDA followed by quenching the enolate with 3.16 mL of methyldiphenylchlorosilane in 0.3 mL of HMPA and 5 mL of THF. The crude product was purified by Kugelrohr distillation, affording 3.13 g (87%) of a 63:37 mixture of C- and O-silylated isomers contaminated with a small amount of starting material: bp 110–115 °C (0.2 mm); IR 1750, 1710, 1660 cm^{-1}, ^{13}C NMR (starting material) δ 170.34, 137.28–126.57, 61.02, 41.14, 13.62, (silyl ketene acetal) δ 143.96, 137.28–126.57, 95.31, 58.85, 18.17, -3.12, (C-silyl ester) δ 172.24, 137.28–126.57, 67.64, 24.94, 14.22; ^{29}Si NMR δ -3.00 (silyl ketene acetal), δ -6.50 (C-silylated isomer); MS (starting material), *m/e* 164 (21), 91 (100), (C/O isomers) *m/e* 360 (not obs), 255 (100).

Reaction of Dimethylphenylchlorosilane with the Lithium Enolate of Ethyl Phenylacetate. Attempted Preparation of Ethyl 2-(Dimethylphenylsilyl)phenylacetate. Via the general procedure, 1.64 g (10 mmol) of ethyl phenylacetate in 5 mL of THF was reacted with 11.5 mmol of LDA followed by quenching the enolate with 1.9 mL (11.5 mmol) of dimethylphenylchlorosilane. The crude product was purified by Kugelrohr distillation, affording 2.68 g (90%) of a 53:47 mixture of C- and O-silylated isomers: bp 109–115 °C (0.4 mm); IR 1725, 1650 cm^{-1}; ^{13}C NMR (C-silyl isomer) δ 175.22, 137.03–126.46, 63.67, 41.30, 14.05, -1.06, (silyl ketene acetal) δ 156.42, 137.03–126.46, 123.43, 60.64, 14.49, -0.68; ^{29}Si NMR δ +10.07 (silyl ketene acetal), +6.53 (C-silyl ester).

Reaction of Methyldiphenylchlorosilane with the Lithium Enolate of Ethyl Phenoxyacetate. Attempted Preparation of Ethyl 2-(Methyldiphenylsilyl)phenoxyacetate. Via the general procedure, 0.76 g (5 mmol) of ethyl phenoxyacetate in 3 mL of THF was reacted with 6.5 mmol of LDA followed by quenching the enolate with 1.03 mL (5 mmol) of methyldiphenylchlorosilane. The crude product was purified by Kugelrohr distillation, affording 0.60 g (82%) of a 63:37 mixture of C-/O-silylated isomers: bp 140–145 °C (0.5 mm); IR 1715, 1665 cm^{-1}; ^{13}C NMR (C-silyl ester) δ 176.79, 137.40–127.49, 67.27, 60.91, 18.19 -4.5, (silyl ketene acetal) δ 159.35, 137.30–127.49, 121.37, 58.91, 18.17, -3.12; ^{29}Si NMR δ -3.19 (silyl ketene acetal), -4.49 (C-silyl ester).

Reaction of Methyldiphenylchlorosilane with the Lithium Enolate of Ethyl Phenoxyacetate Using HMPA as Cosolvent. Attempted Preparation of Ethyl 2-(Methyldiphenylsilyl)-phenoxyacetate. Via the general procedure, 0.76 g (5 mmol) of ethyl phenoxyacetate in 3 mL of THF was reacted with 6.5 mmol of LDA followed by quenching the enolate with 1.03 mL (5 mmol) of methyldiphenylchlorosilane in 0.2 mL of HMPA and 5 mL of THF. The crude reaction product was analyzed without further purification: IR 1715, 1665 cm^{-1}; C/O ratio 60/40; ^{29}Si NMR δ -3.15 (silyl ketene acetal), -4.45 (C-silyl ester).

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Registry No. **2a**, 59344-14-8; **2b**, 112197-34-9; **2d**, 112197-38-3; **2** (R^1 = H, R^2 = Ph, R^3 = Et, SiR_3 = $SiMe_2Ph$), 112197-36-1; **3a**, 13950-57-7; **3b**, 87776-13-4; **3c**, 77772-21-5; **3d**, 112197-18-9; **3e**, 112197-19-0; **4a**, 77772-22-6; **4b**, 112197-21-4; **4c**, 112197-22-5; **4d**, 77772-28-2; **4e**, 89638-15-3; **4f**, 112197-23-6; **4g**, 99165-44-3; **4h**, 89638-16-4; **4i**, 89968-59-2; **4j**, 99165-46-5; **4k**, 112197-24-7; **4l**, 112197-25-8; **4m**, 112197-26-9; **4n**, 112197-27-0; **6**, 112197-33-8; **7a**, 91413-17-1; **7b**, 99165-47-6; **7c**, 99165-48-7; **7d**, 91586-15-1; **7e**, 112197-28-1; **7f**, 112197-29-2; **8a**, 112197-30-5; **8b**, 112197-31-6; **10a**, 77772-24-8; **10b**, 112197-32-7; **10c**, 101773-27-7; (*R*)-(-)-**12**, 112197-20-3; (-)-**11**, 51042-11-6; **13** (diastereomer 1), 112219-57-5; **13** (diastereomer 2), 112197-43-0; $Ph_2MeSiCl$, 144-79-6; CH_3CO_2Et, 141-78-6; CH_3CO_2-*i*-Pr, 108-21-4; CH_3CO_2-*t*-Bu, 540-88-5; $CH_3C(O)O_2C_3H_5$, 591-87-7; (*S*)-(-)-1-NpPhMeSiCl, 960-82-7; $CH_3CH_2CO_2Et$, 105-37-3; $CH_3CH_2CO_2$-*i*-Pr, 637-78-5; $CH_3CH_2CO_2C_3H_5$, 2408-20-0; $CH_3CH_2CO_2$-*t*-Bu, 20487-40-5; $CH_3CH_2CH_2CO_2Et$, 105-54-4; $CH_3CH_2CH_2CO_2$-*t*-Bu, 2308-38-5; $CH_3CH_2CH_2CH_2CO_2Et$, 539-82-2; *n*-$C_8H_{17}CH_2CO_2Et$, 110-38-3; $CH_2{=}CH(CH_2)_7CH_2CO_2Et$, 692-86-4; *n*-$C_{16}H_{33}CH_2CO_2Et$, 111-61-5; $C_3H_5CH_2CO_2Et$, 1968-40-7; $CH_3C(O)CH_2CH_2CO_2Et$, 539-88-8; $CH_3C(O)CH_2CH_2CH_2CO_2Et$, 13984-57-1; $(CH_3)_2CHCO_2Et$, 97-62-1; $\overline{CH_2CH_2}CHCO_2Et$, 4606-07-9; $\overline{CH_2CH_2CH_2}CHCO_2Et$, 14924-53-9; $(CH_3)_2CHCO_2Me$, 547-63-7; $PhCH_2CO_2Et$, 101-97-3; $PhCH(SiMe_2Ph)CO_2Et$, 112197-35-0; $PhOCH_2CO_2Et$, 2555-49-9; $PhOCH(SiMePh_2)CO_2Et$, 112197-37-2; $EtO_2CCH_2CH_2CO_2Et$, 123-25-1; $(EtO)(Ph_2MeSiO)C{=}CHCH{=}C(OEt)(OSiMePh_2)$, 112197-39-4; $CH_3CH{=}CHCO_2Et$, 10544-63-5; $CH_2{=}CHCH{=}C(OEt)(OSiMePh_2)$, 112197-40-7; $CH_2(CO_2Et)_2$, 105-53-3; $EtO_2CCH{=}C(OEt)(OSiMePh_2)$, 112197-41-8; 2,6-di-*tert*-butylphenyl acetate, 79280-90-3; dihydro-2(3*H*)-furanone, 96-48-0; 3(*H*)-dihydro-5-methyl-2-furanone, 108-29-2; *cis*-hexahydro-2-(3*H*)-benzofuranone, 24871-12-3; δ-valerolactone, 542-28-9; ϵ-caprolactone, 502-44-3; [(3,4-dihydro-2*H*-pyran-6-yl)oxy]methyldiphenylsilane, 108999-19-5; [(2,3,4,5-tetrahydro-oxepin-7-yl)-oxy]methyldiphenylsilane, 112197-42-9; dimethylphenylchlorosilane, 768-33-2.

Supplementary Material Available: The physical and spectroscopic data not described in the Experimental Section (13 pages). Ordering information is given on any current masthead page.