presence of the *N*-(phenylsulfonyl) group, comparison of the chemical shifts and carbonyl stretches with analogous natural products was uninformative.

The structural assignments for **8**, **9**, **10**, and **11** were ultimately made after single-crystal analyses of lactone **10** and lactams **9** and **11** (see supplementary material for details).[11] The formation of the [3.2.1]bicyclic lactone **10** can be readily explained by the initial DiBAL reduction of the lactone carbonyl of **7** to the lactol followed by a ring opening to an aldehyde/thioester system, which undergoes a new ring closure of the sulfonamide anion onto the aldehyde carbonyl and expulsion of a thiomethyl group to form the amido acetal unit of **10**. This unusual series of events is just one manifestation of the unusual reactivity of the carbon atom bearing three different heteroatoms in **7**.

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Supplementary Material Available: Summary of crystal data, fractional coordinates, thermal parameters, bond distances and angles, and perspective drawings for compounds **9**, **10**, and **11** and spectral characterization for compounds **7a**, **7b**, **8**, **9**, **10**, and **11** (27 pages). Ordering information is given on any current masthead page.

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[11] Lactone **10** crystallized in the monoclinic space group $P2_1/c$, with a = 10.581 (2) Å, b = 9.157 (3) Å, c = 16.395 (5) Å, and β = 98.50 (2)°. The structure was solved with direct methods and refined to a R = 0.045 with a final R_w of 0.037. Lactam **9** crystallized in a nonstandard space group $I2/a$, with a = 18.716 (6) Å, b = 8.486 (4) Å, c = 21.237 (4) Å, and β = 98.26 (2)°. The structure was refined to a R = 0.040 with a final R_w = 0.037. Lactam **11** crystallized in the monoclinic space group $P2_1/c$, with a = 8.428 (3) Å, b = 8.586 (5) Å, c = 22.786 (13) Å, and β = 98.70 (4)°. The structure was solved with direct methods and refined to a R = 0.047 with a final R_w = 0.041.

A New Alkyllithium Reagent for the Direct Conversion of Aldehydes and Ketones to Vinylsilanes

Summary: [(Methoxydimethylsilyl)(trimethylsilyl)methyl]lithium (**1**), which is readily formed in hydrocarbon solvent from silane **2** and *tert*-butyllithium, reacts with carbonyl compounds to yield the corresponding alkenylsilanes **3** via a Peterson-type reaction.

Sir: The vinylsilane group is a highly versatile synthon in organic synthesis.[1,2] In addition to serving as a latent carbonyl,[3] the trimethylsilyl group of alkenylsilanes can be replaced by a number of electrophiles to yield substituted alkenes. These reactions are generally of high yield and stereospecific.[2] Other net substitution reactions replace the trimethylsilyl group with alkyls, yielding either one of two possible isomers stereospecifically depending on the reaction conditions.[4] More recently 2,2-disubstituted alkenylsilanes have been shown to be precursors to alkylidene carbenes.[5]

Scheme I

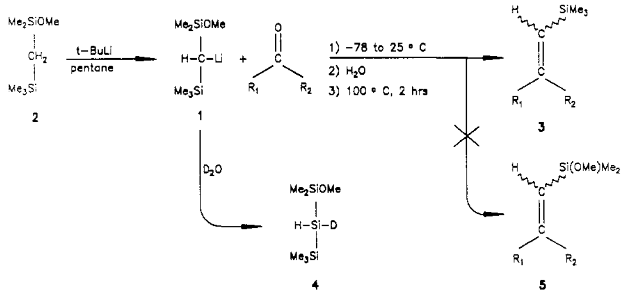

Table I. Yields and Isomer Ratios of Alkenylsilanes $R_1(R_2)C{=}C(H)SiMe_3$

carbonyl compound	product	R_1	R_2	yield, %[a]	*E*:*Z*
cyclohexanone	**3a**	$-(CH_2)_5-$		68[b]	
2-cyclohexen-1-one	**3b**	$-CH{=}CH(CH_2)_3-$		61[c]	2:1
3-pentanone	**3c**	Et	Et	70[c]	
benzaldehyde	**3d**	Ph	H	85[d,e]	3:1

[a] Isolated yields. [b] See ref 10 and 11. [c] Spectral and analytical data available in supplementary material. [d] Quantitative by NMR. [e] See ref 21.

Although there are a number of routes to vinylsilanes,[1,2,6,7] these have some important limitations. Since most of the reported syntheses utilize an alkyne,[2,8,9] only in rare cases have exocyclic alkenylsilanes been obtained.[10–12] [Bis(trimethylsilyl)methyl]lithium, the logical precursor to alkenylsilanes via the Peterson methodology,[13] is only effective with nonenolizable aldehydes and ketones.[14] We now report on a new lithium reagent, [(methoxydimethylsilyl)(trimethylsilyl)methyl]lithium (**1**),

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[9] For some more recent references, see: Chatani, N.; Takeyasu, T.; Nobuhiko, H.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539.

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which converts carbonyl groups to vinylsilane groups, even in enolizable compounds.

Lithium reagent **1** is formed in quantitative yield by the regiospecific lithium–hydrogen exchange of (methoxydimethylsilyl)(trimethylsilyl)methane (**2**) with *tert*-butyllithium in hydrocarbon solvent at room temperature (see Scheme I). This was confirmed by quenching of **1** with D_2O, which gave the monodeuterated product **4** in 98% yield based on **2**.[15] Notably the formation of **1** is not complicated by substitution reactions at the methoxy-substituted silicon atom or by metalation at the silyl methyl groups under these conditions. As we reported previously,[16] compound **2** is readily obtained by trapping [(methoxydimethylsilyl)methyl]lithium with trimethylchlorosilane.

As shown in Table I, **1** reacts with each of the carbonyl compounds in this study (cyclohexanone, 2-cyclohexen-1-one, 3-pentanone, and benzaldehyde) to produce good yields of the corresponding alkenylsilane. In each case,[17] **1** was prepared by adding a pentane solution of *tert*-butyllithium to a solution of **2**. The reaction mixture was cooled to −78 °C and the carbonyl compound was added dropwise. The reaction mixture was allowed to warm slowly with stirring to room temperature overnight. An aqueous workup was followed by removal of the solvent and heating of the crude product for 2 h at 100 °C. Flash chromatography yielded the alkenylsilane **3**.

When the ketone was added at 0 °C or in the presence of diethyl ether, the yield of the alkenylsilane was reduced. Analysis of the crude product before chromatography by ^{13}C NMR indicated the absence of the other possible olefin, **5**, derived from elimination of the trimethylsilyl group. This result is consistent with the increased electrophilicity of silicon on replacement of alkyl groups with alkoxy groups.[18]

In a few instances for reactions with cyclohexanone, an additional unidentified compound was observed. This compound was cleanly converted to the alkenylsilane upon heating to 100 °C for 2 h. Although apparently an intermediate, the ^{13}C NMR data is not consistent with the anticipated β-hydroxy silane intermediate.[19] Work is currently in progress to identify this intermediate and to study the conditions under which it may be isolated reproducibly. In any case, the desired alkenylsilane **3a** was produced exclusively after heating.

Treatment of reagent **1** with 2-cyclohexen-1-one or benzaldehyde resulted in a mixture of *E* and *Z* isomers. The stereochemical assignments were made on the basis of 300-MHz ^1H NMR spectra. The fair selectivity for the reaction with cyclohexenone (2:1, *E*:*Z*)[20] and with benzaldehyde (3:1, *E*:*Z*)[21] contrasts with the lack of stereoselectivity generally observed with other Peterson-type olefinations.

The effectiveness of the described procedure with enolizable compounds should make available many useful, but previously unattainable, alkenylsilanes. Efforts are currently underway to isolate and identify reaction intermediates and to establish the mechanism of these and related reactions.

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Supplementary Material Available: Spectral and analytical data for new compounds **3b** and **3c** shown in Table I (2 pages). Ordering information is given on any current masthead page.

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[15] The yield was determined by integration of the methylene carbon resonances, in the proton-decoupled ^{13}C NMR spectra, of **3** and **4**, which appear as a singlet at 4.1 ppm and a 1:1:1 triplet at 3.7 ppm, respectively.

[16] Bates, T. F.; Thomas, R. D. *J. Organomet. Chem.* **1989**, *359*, 285.

[17] Using the reaction with cyclohexanone as a typical example: 12.0 mmol of *tert*-butyllithium (7.06 mL, 1.7 M in pentane) was added to 12.0 mmol of **2** in 15 mL of dry pentane. After being stirred for 2 h, the reaction mixture was cooled to −78 °C and 10.0 mmol of cyclohexanone was added dropwise by syringe. The reaction mixture was allowed to warm slowly to room temperature while being stirred overnight. This was hydrolyzed with 15 mL of saturated NH_4Cl followed by washing with 15 mL of H_2O, extraction of the aqueous portions with 10 mL of pentane, and drying of the combined organic fractions with $MgSO_4$. After removal of the solvent, the crude product was heated for 2 h at 100 °C. Flash chromatography (silica gel/pentane) yielded 1.15 g (68%) of **3a**.

[18] Eaborn, D. *Organosilicon Compounds*; Butterworths: London, 1960; p 301.

[19] The unidentified compound was observed by NMR in several reactions following the aqueous workup. ^{13}C NMR: −1.0, 1.0, 22.5, 23.0, 25.0, 28.0, 31.0, 119.0, 135.5 ppm.

[20] A complete listing of the ^1H NMR chemical shifts and the vinylic proton coupling patterns and coupling constants is included in the supplementary material.

[21] The stereochemical assignments were made by comparing the ^1H NMR spectra to those previously reported for each isomer. Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520.

An Organozinc Aid in Alkylation and Acylation of Lithium Enolates

Summary: The presence of dimethylzinc in the reaction of lithium enolates and electrophiles effectively suppresses undesired α-proton exchange reaction and enhances the efficiency of enolate alkylation and acylation.

Sir: Reaction of lithium enolates and electrophiles is one of the most fundamental synthetic operations.[1] The utility, however, is often hampered by undesired proton exchange between the starting enolates and ketonic products. For example, enolates of ketones such as cyclopentanones containing highly acidic protons are prone to undergo polyalkylation reactions with alkyl halides,[1,2] and also the yields of the C-acylation products with acyl halides hardly exceed 50% because of the high acidity of the resulting β-dicarbonyl compounds,[1a,3] We here report

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[1] Reviews: (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972; Chapters 9–11. (b) Augustine, R. L. *Carbon-Carbon Bond Formation*; Marcel Dekker: New York, 1979; Vol. 1.

[2] For some examples, see: (a) Tardella, P. A. *Tetrahedron Lett.* **1969**, 1117. (b) House, H. O.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1971**, *36*, 2361. (c) Borowitz, I. J.; Casper, E. W. R.; Crouch, R. K.; Yee, K. C. *Ibid.* **1972**, *37*, 3873. (d) Posner, G. H.; Sterling, J. J.; Whitten, C. E.; Lentz, C. M.; Brunelle, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 107.

[3] Review: Hauser, C. R.; Swamer, F. W.; Adams, J. T. *Org. React.* **1954**, *8*, 59.

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