Tetrahedron Letters No. 2, pp 159 - 162, 1977. Pergamon Press. Printed in Great Britain.

DIRECT CONVERSION OF KETONES TO VINYLSILANES, -GERMANES, AND -STANNANES

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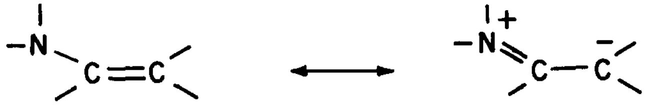
(Received in USA 4 October 1976; received in UK for publication 30 November 1976)

The synthetic utility of enamines (1) is derived in large part from their ready availability via the condensation of aldehydes and ketones with secondary amines,[2-4] and their intrinsic mesomeric nature which negatively polarizes the β-carbon atom (*cf* 2) and facilitates electrophilic attack at that site.[5] Although carbon is more electronegative (2.55) than silicon (1.90) and other Group IV elements (e.g., Ge and Sn), d_π-p_π electron withdrawal in vinyl derivatives of these metals (such as 3) provides for polarization in the opposite sense (4).[6] Exploitation of the latent potential for synthesis conveyed by such "reversed" polarization has in our opinion been limited by the absence of a general synthetic approach to vinylsilanes and their congeners. Certainly, syntheses based upon methyllithium condensations with R_3MX,[7] 1,2-addition reactions of R_3MCH_2MgX and subsequent dehydration,[8] $LiAlH_4$ reductions of $R_3MC{\equiv}CCH_2OH$,[9] base-promoted cleavage reactions and eliminations,[10] and controlled hydroboration of $R'C{\equiv}CSiR_3$[11] have contributed to the advancement of this field. But the exceptionally varied nature of the starting materials and their frequently indirect availability do not hold promise for universal adaptation. This note reports a potential solution to this problem in the form of a simple two-step conversion from ketonic precursors.



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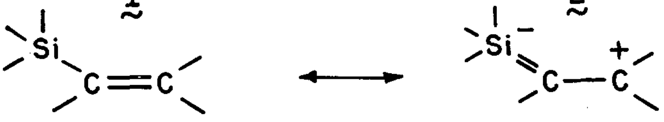

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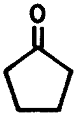
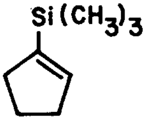
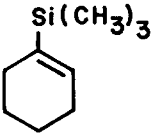
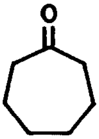
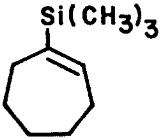
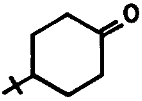
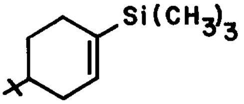
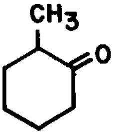
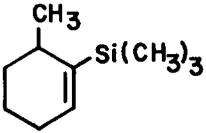
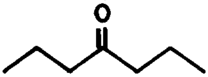
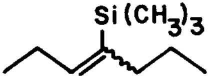
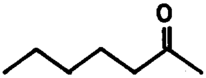
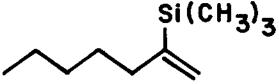
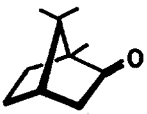
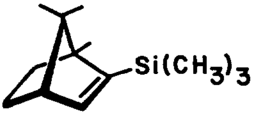
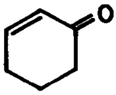
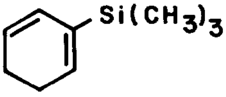
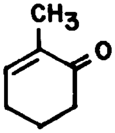
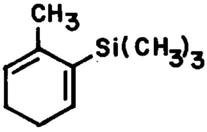
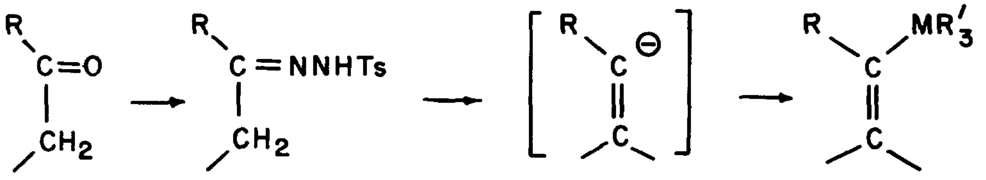
The present approach takes advantage of the proclivity of tosylhydrazones for conversion to vinyl carbanion intermediates upon treatment with four equiv of *n*-butyllithium in TMEDA

Table I. Summary of Ketone Enesilylations

Ketone	Vinylsilane	Yield, %[a]	^{1}H NMR (δ)[b]
		50	(CCl$_4$) 6.00 (m, 1), 2.71-2.23 (m, 4), 2.23-1.69 (m, 2), and 0.21 (s, 9).
		68	(C$_6$D$_6$) 6.12 (m, 1), 2.12 (m, 4), 1.72 (m, 4), and 0.22 (s, 9).
		62	(CDCl$_3$) 6.23 (m, 1), 2.53-2.13 (m, 4), 2.13-1.31 (m, 6), and 0.18 (s, 9).
		71	(C$_6$D$_6$) 6.14 (m, 1), 2.46-1.06 (m, 7), 0.99 (s, 9), and 0.24 (s, 9).
		61	(CDCl$_3$) 6.05 (m, 1), 2.4-1.3 (m, 7), 1.05 (d, J = 7 Hz, 3), and 0.18 (s, 9).
		38	(CDCl$_3$) 5.76 (t, J = 7 Hz, 1), 2.44-1.90 (m, 4), 1.74-1.24 (m, 2), 1.24-0.67 (m, 6), and 0.15 (s, 9).
		26	(CDCl$_3$) 5.59 (m, 1), 5.34 (d, J = 1.5 Hz, 1), 2.29-1.85 (m, 2), 1.77-1.15 (m, 6), 1.15-0.73 (m, 3), and 0.18 (s, 9).
		15	(C$_6$D$_6$) 6.30 (d, J = 1.5 Hz, 1), 2.32 (t, J = 1.5 Hz, 1), 2.03-1.30 (m, 3), 1.23 (s, 3), 1.20-1.00 (m, 1), 0.94 (s, 3), 0.84 (s, 3), and 0.24 (s, 9).
		40	(C$_6$D$_6$) 6.29-5.60 (m, 3), 2.03 (m, 4), and 0.15 (s, 9).
		44	(C$_6$D$_6$) 6.28 (m, 1), 5.59 (m, 1), 1.95 (m, 7), and 0.22 (s, 9).

[a] The cited yields represent those obtained from the tosylhydrazones; all reactions were conducted on 1-2 g of sample and the yields refer to pure vinylsilane isolated after preparative vpc on an SF-96 column. [b] Spectra were recorded on a Varian T-60 NMR spectrometer with benzene as internal standard; the particular solvent employed is given in parentheses.

solution[12] and the ready in situ reaction of these anions with commercially available $(CH_3)_3MX$ reagents. Various examples involving trimethylsilyl chloride as the electrophilic reagent are given in Table I. Importantly, the $(CH_3)_3Si$- group becomes bonded exclusively to the original carbonyl carbon (see Scheme). An additional attractive feature is found in the regioselectivity of the reaction. In the case of 2-heptanone, for example, electronic (and also steric)[13] factors are conducive to vinyl anion generation by abstraction of a methyl, and not a methylene, proton. The resulting vinylsilane is consequently the terminal isomer. Likewise, deprotonation of cyclic enone tosylhydrazone anions is directed almost completely to the α' site,[14] with the result that the position of the original carbon-carbon double bond is maintained.[13] In all cases, the reactions were clean. Although the experiments herein described were conducted on somewhat limited quantities, our experience indicates that scale-up should present no particular problem.

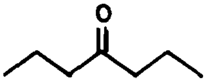
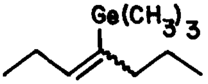
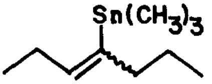
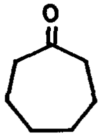
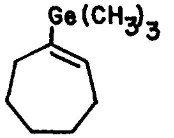
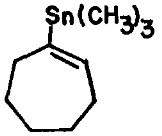
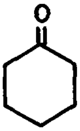
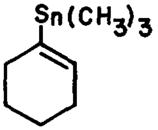
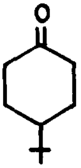
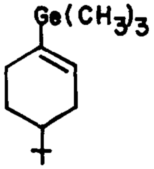


The versatility of the procedure is signaled by its ready adaptability to the preparation of vinylgermanes and vinylstannanes (Table II). All of the reaction products were characterized by ^1H NMR spectroscopy in addition to combustion analysis (if previously unknown). There appear to be no significant differences in the three groups of reactions. Although there is a clear limitation on the scope of this synthesis as the direct result of the need for alkyllithium utilization, the method promises to be convenient and efficient for a wide variety of cases. The chemistry of these unsaturated organometallics is currently under active study.

The following procedure provides additional detail relating to the preceding discussion.[15]

1-Trimethylsilylcycloheptene. A solution of cycloheptanone tosylhydrazone (1.5 g, 5.35 mmol) in TMEDA (50 ml) was cooled to -78° and treated while under nitrogen with 4 equiv of *n*-butyllithium (9.34 ml of 2.29 *M* in hexane). The deep red solution was stirred at -78° for 10 min and allowed to warm to room temperature. After 2 hr, trimethylsilyl chloride (2.33 g, 21.4 mmol) was introduced to the cooled (0°) solution via syringe. The resulting mixture was stirred for 15 min prior to the addition of water (10 ml) and extraction with ether. The organic phase was washed with water and the combined aqueous layers reextracted with ether. After washing with saturated copper sulfate and sodium chloride solutions, the ether layer was dried and concentrated to a volume of *ca* 6 ml by careful distillation through a Vigreux column. The residual material was vacuum transferred and subjected to preparative vpc purification (SF-96, 85°). There was obtained 0.56 g (62%) of the title compound.

Table II. Preparation of Vinylgermanes and -stannanes.

Ketone	Vinylgermane	Yield, %[a]	Vinylstannane	Yield,%[a]
		47		43
		64		56
				47
		58		

[a] See footnote a of Table I.

FOOTNOTES AND REFERENCES

(1) (a) Dissertation Fellow, 1975-1976; (b) Undergraduate Research Participant, 1975-1976.

(2) C. Mannich and H. Davidson, Ber., B69, 2106 (1936).

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(5) "Enamines: Synthesis, Structure, and Reactions," A. G. Cook, Ed., Marcel Dekker, New York, 1969.

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(7) Leading references: J. J. Eisch and G. A. Damasevitz, J. Org. Chem., 41, 2214 (1976); K. Uchida, K. Utimoto, and H. Nozaki, ibid., 41, 2215 (1976).

(8) F. A. Carey and J. R. Toler, J. Org. Chem., 41, 1966 (1976), and relevant references cited therein.

(9) G. Stork, M. E. Jung, E. Colvin, and Y. Noel, J. Am. Chem. Soc., 96, 3684 (1974). Silane additions to acetylenes are also well recognized reactions.

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(12) (a) J. E. Stemke and F. T. Bond, Tetrahedron Lett., 1815 (1975); (b) J. E. Stemke, A. R. Chamberlin, and F. T. Bond., ibid., 2947 (1976); (c) P. C. Traas, H. Boelens, and H. J. Takken, ibid., 2287 (1976).

(13) Regiospecificity is seemingly dependent also upon tosylhydrazone stereochemistry, at least in certain cases: R. H. Shapiro, M. F. Lipton, K. J. Kolonko, R. L. Buswell, and L. A. Capuano, Tetrahedron Lett., 1811 (1975); W. G. Dauben, G. T. Rivers, W. T. Zimmerman, N. C. Yang, B. Kim, and J. Yang, ibid., 2951 (1976).

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(15) The partial financial support of the National Science Foundation and the National Institutes of Health is gratefully acknowledged.