Registry No. 4, 15186-48-8; *ent*-**4**, 22323-80-4; **5**, 81277-28-3; *ent*-**5**, 81277-29-4; **9**, 81277-30-7; **10**, 81277-31-8; **11**, 81277-32-9; **12**, 81277-33-0; **13**, 81277-34-1; **14**, 58521-45-2; **15** (major isomer), 81277-35-2; **15** (minor isomer), 81277-36-3; **16**, 58521-49-6; **17**, 81277-37-4.

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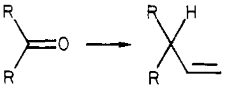
[β-(Trimethylsilyl)ethyl]lithium: A New Reagent for Carbonyl Reductive Vinylation

Summary: The direct transformation of a carbonyl compound into a vinyl compound (i.e., cyclohexanone → vinylcyclohexane) is now possible with use of the new reagent described in this paper: [β-(trimethylsilyl)ethyl]lithium, followed by protodesilylation.

Sir: The direct transformation of a carbonyl group **1** into a vinyl compound **2** (eq 1) has not been possible directly.[1] This transformation can now readily be accomplished with use of the new reagent reported in this paper: [β-(trimethylsilyl)ethyl]lithium (**3a**).



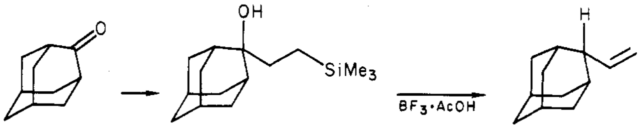
1 2 (1)

$Me_3SiCH_2CH_2M$ $Me_3SiCH_2\overset{+}{C}H_2$ $Me_3SiCH_2\bar{C}H_2$

3a, M = Li
3b, M = MgBr
4
5

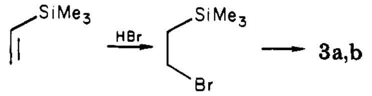
These reagents correspond to an "umpolung"[3] of the well-recognized[4] β-(trimethylsilyl) carbonium ion chemistry (cf. **4**), since they formally represent β-(trimethylsilyl) anions **5**.[5,9–11] As such, ready and high yield addition to carbonyl electrophiles is observed.

For example, addition of 2-adamantanone (**6**) to **3a** in ether (−78 °C) gives alcohol **7** quantitatively (72% isolated).[12] Our expectation[13] that acid treatment of **7** would lead to dehydration to an allylsilane and subsequent protonolysis to vinyl compound **8** was indeed the case. $BF_3 \cdot AcOH$ treatment of **7** gives olefin **8** (100%, CH_2Cl_2, 25 °C, 5 min). Other results with aldehydes and ketones are collected in Table I. In most cases the alcohols were purified by column chromatography. NMR signals at δ = 0 (Me_4Si) and a multiplet at δ 0.2–0.8 (CH_2CH_2) were observed.



6 7 8

This compound is readily prepared from the corresponding bromide[14] **9** and *tert*-butyllithium at −78 °C (eq 2). For large-scale preparations the Grignard reagent **3b** is more convenient (Mg, ether, 25 °C). While lithium reagent **3a** has been generated and used in situ, Grignard **3b** has been prepared on a 0.5-mol scale, and stock solutions have been stored at 0 °C for weeks. Compound **9** is labile, decomposing to Me_3SiBr and (presumably) ethylene on standing at 25 °C overnight. It is best used immediately after washing with H_2O and drying over silica gel (which also removes Me_3SiBr seen as a singlet at δ 0.2).



9 (2)

An interesting observation of possible theoretical interest is the behavior of Grignard **3b** with hindered ketones. The known ketone reduction[15] by the Grignard reagent via β-hydrogen transfer is particularly pronounced in the case of **3b** wherein 35% **7** and 65% **10** are produced. However, Grignard **11**, sterically similar to **3b**, gave no reduction of **6**. Thus it seems that the β-hydrogen transfer from a carbon bearing a Me_3Si group is especially favorable.

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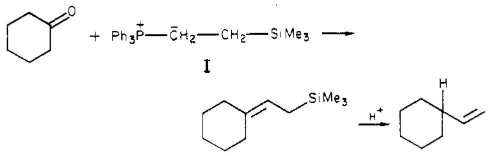
(1) This transformation via the Wittig reagent I[2] has been reported; however, the reagent I reacts in good yield only with aldehydes and cyclohexanone. Fleming, I.; Paterson, I. *Synthesis* **1979**, 446–448. This general transformation is known for arylation: Hall, S. S.; McEnroe, F. J. *J. Org. Chem.* **1975**, *40*, 271–275.



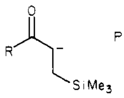
I

(2) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104–3106.

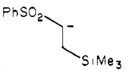
(3) Seebach, D.; Kolb, M. *Chem. Ind.* (*London*) **1974**, 687–692.

(4) (a) Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A.* **1970**, *6*, 153–207. (b) Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442–448.

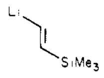
(5) Other anions β to silicon have been reported. A variety of ketone stabilized β-(trimethylsilyl) anions such as II have been produced by the conjugate addition of Me_3SiLi to enones.[6] Sulfone anion III has been reported[7] as well as ylide I.[2] [β-(Trimethylsilyl)vinyl]lithium (IV) is known.[8]



II



III



IV

(6) Still, W. C. *J. Org. Chem.* **1976**, *41* 3063–3064.

(7) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649–2650.

(8) Cunico, R. F.; Clayton, J. F. *J. Org. Chem.* **1976**, *41*, 1480–1482.

(9) β-(Triphenylsilyl)ethyl Grignard V has been studied: (a) Bourne,

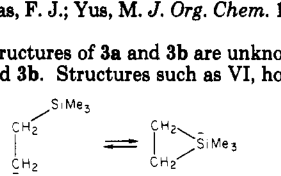
$$Ph_3SiCH_2CH_2MgBr$$

V

A. J.; Rowley, R. J. *J. Org. Chem.* **1972**, *39*, 93–97. (b) Jarvie, A. W. P.; Bourne, A. J.; Rowley, R. J. *J. Organomet. Chem.* **1972**, *39*, 93–97.

(10) Cf. a series of papers on β-substituted organolithium compounds: Barluenga, J.; Fananas, F. J.; Yus, M. *J. Org. Chem.* **1979**, *44*, 4798–4801 and references cited.

(11) The actual structures of **3a** and **3b** are unknown. They are only represented as **3a** and **3b**. Structures such as VI, however, have precedence in silicon and especially tin chemistry: cf. Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290–1303.



VI

(12) All new compounds reported in this paper possessed spectral data and combustion analysis in accord with their structures.

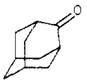
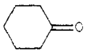
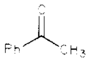
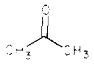
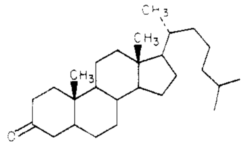
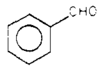
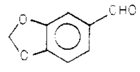
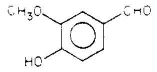
(13) While this work was in progress a report appeared of a similar dehydration/rearrangement of a large set of γ-(trimethylsilyl) carbinols. These alcohols were made by "classical" methods: Fleming, I.; Patel, S. K. *Tetrahedron Lett.* **1981**, 2321–2324.

(14) Somner, L. H.; Bailey, D. L.; Goldberg, G. M.; Buck, C. E.; Bye, T. S.; Evans, F. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1954**, *76*, 1613–1618.

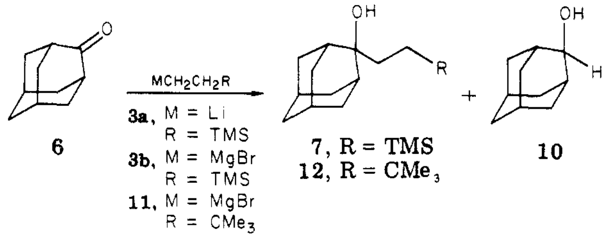
(15) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; American Chemical Society: Washington, DC, 1976; p 177 ff.

0022-3263/82/1947-1983$01.25/0

Table I. Addition of β-(Trimethylsilyl) Anions to Carbonyl Groups

entry	substrate	alcohol yield, %	olefin yield, %
1		35[a] 72[b]	100
2		70 (mp 37-40 °C)	95
3		65	72[c]
4		81	100[c]
5		(mp 153-156 °C)	97[d] (mp 66-69 °C)
6	$CH_3(CH_2)_5CHO$	90	
7		84	
8	 piperonal	88	43 safrole
9	 vanillin	85[e]	60 eugenol

[a] Via RMgX (3b) major product was reduction. [b] Via RLi (3a). [c] Reference 13. [d] Overall from cholestanone. [e] Two equivalents of 3b used.



The new silicon reagents **3a** and **3b** make readily available many γ-functionalized silicon compounds; in addition, the carbonyl reductive vinylation strategy leads to unique synthetic applications such as the synthesis of safrole from piperonal and eugenol from vanillin (Table I). We are actively exploring extensions of this chemistry.

Acknowledgment. We thank the National Institutes of Health (GM-29259) for financial support.

Registry No. 3a, 81372-25-0; **3b**, 81372-26-1; **6**, 700-58-3; **7**, 81372-27-2; **8**, 81372-28-3; **9**, 18156-67-7; **10**, 700-57-2; cyclohexanone, 108-94-1; 1-[2-(trimethylsilyl)ethyl]cyclohexanol, 81372-29-4; vinylcyclohexane, 695-12-5; acetophenone, 98-86-2; 2-phenyl-4-(trimethylsilyl)-2-butanol, 18410-35-0; 3-phenyl-1-butene, 934-10-1; acetone, 67-64-1; 2-methyl-4-(trimethylsilyl)-2-butanol, 4426-65-7; 3-methyl-1-butene, 563-45-1; 5α-cholestan-3-one, 566-88-1; 3-hydroxy-3-[2-(trimethylsilyl)ethyl]-5α-cholestane, 81372-30-7; 3-vinyl-5α-cholestane, 81372-31-8; heptanal, 111-71-7; 1-(trimethylsilyl)-3-nonanol, 81372-32-9; benzaldehyde, 100-52-7; 1-phenyl-3-(trimethylsilyl)-1-propanol, 54288-07-2; piperonal, 120-57-0; 5-[1-hydroxy-3-(trimethylsilyl)prop-1-yl]-1,3-benzodioxole, 81372-33-0; safrole, 94-59-7; vanillin, 121-33-5; 1-[(4-hydroxy-3-methoxy)phenyl]-3-(trimethylsilyl)propan-1-ol, 81391-19-7; eugenol, 97-53-0.

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