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TRANSITION-METAL CATALYZED REGIOSELECTIVE ADDITION OF $PhMe_2SiBEt_3Li$ AND Bu_3SnBEt_3Li TO ACETYLENIC COMPOUNDS IN THE PRESENCE OF METHANOL

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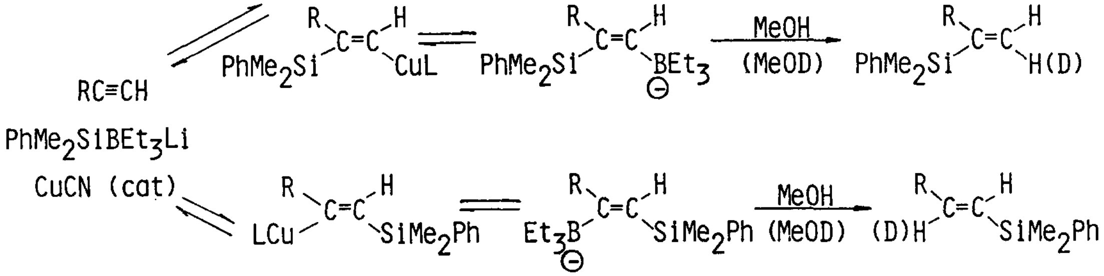
Abstract: Treatment of acetylenic compounds with $PhMe_2SiBEt_3Li$ in the presence of a transition-metal catalyst affords vinylsilanes in good yields. Coexistence of methanol as a proton source is essential for the completion of the reaction.

Extensive studies have been explored with the reactions of organoboron compounds such as hydroboration or haloboration.[1] Several compounds containing B-Si bond have been synthesized;[2] nevertheless, no examples are known for their synthetic utility. Here we wish to report that silylboron and stannylboron compounds, $PhMe_2SiBEt_3Li$ and Bu_3SnBEt_3Li, add to triple bonds effectively to give vinylsilanes or vinylstannanes, respectively, under good control of the regio- and stereoselectivity.[3]

The reaction of 1-dodecyne with 2 equiv. of $PhMe_2SiBEt_3Li$ in the presence of a catalytic amount of CuCN afforded a mixture consisting of the starting material (35% recovery) and the desired vinylsilanes (1-dimethylphenylsilyl-1-dodecene:2-silyl isomer = 64:36, 50% combined yield) after quenching the reaction mixture with 1N HCl. Prolonged reaction time could not improve the conversion. In contrast, treatment of propargyl alcohol under the same reaction conditions provided (E)-3-dimethylphenylsilyl-2-propen-1-ol as a single product in 87% yield. These results indicated that (1) the reaction of acetylenic compounds with $PhMe_2SiBEt_3Li$ is reversible, and the equilibrium favors only marginally the intermediate vinylborate,[4] and (2) in the presence of a proton source, the equilibrium is shifted to the right by protonation of the intermediate. Thus, it was anticipated that the addition of methanol to the reaction mixture of 1-dodecyne and $PhMe_2SiBEt_3Li$ would force the reaction go to completion, and this was indeed the case. Water, diethyl malonate, and phenol were also effective to complete the reaction.[5] We are tempted to assume the following reaction scheme. Weak acids such as water, methanol, and phenol react easily only with the intermediary vinylcopper compound or vinylborate, but are reluctant to react with the silylborate as well as with dimethylphenylsilylcopper reagents.[6]

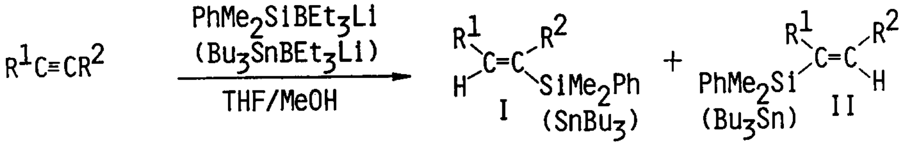


A typical procedure follows. The addition of a hexane solution of triethylborane[7] (1.0 M, 2.0 ml, 2.0 mmol) to a greenish black THF solution of $PhMe_2SiLi$ (0.75 M, 2.7 ml, 2.0 mmol) at 0°C gave a decolorized pale brown solution. Its ^{11}B-NMR spectrum showed a signal at -36.8 ppm, the high field shift of which (Et_3B: 68.5 ppm) reveals the formation of the ate complex, $PhMe_2SiBEt_3Li$.[8] A catalytic amount of CuCN (0.1 mmol) was added, and the color of the solution immediately changed to black. Then a solution of 1-dodecyne (0.17 g, 1.0 mmol) and methanol (0.41 ml, 10 mmol)[9] in THF (2 ml) was added, and the whole was stirred at 25°C for 1 h. Extractive workup (AcOEt, 1N HCl) and purification by preparative tlc on silica gel gave a mixture of 1- and 2-dimethylphenylsilyl-1-dodecene in 89% combined yield (1-silyl isomer:2-silyl isomer = 61:39). Representative results are summarized in Table 1.

CuI, $CuBr{\cdot}SMe_2$, and $CoCl_2(PPh_3)_2$ (the latter for terminal acetylenes only) also catalyze the reaction, while $Pd(PPh_3)_4$, $RuCl_2(PPh_3)_3$, and $NiCl_2(PPh_3)_2$ are not effective. The addition proceeds in cis fashion exclusively. The regioselectivity of the reaction heavily depends on the nature of the catalyst employed. $CoCl_2(PPh_3)_2$ gives exclusively the 1-silyl-1-alkene starting from 1-alkynes. Acetylenic compounds containing a hydroxyl group provide vinylsilanes selectively which have the silyl group on the carbon remote from the hydroxyl group.

The reaction has been extended to stannylboration of acetylenes. The results are also shown in Table 1. The uncatalyzed reaction of stannylboron compounds with acetylenes proceeded very slowly to give vinylstannanes in low yield (entry 14).[11] Catalysts such as CuCN and $CoCl_2(PPh_3)_2$ were effective for this reaction.[12]

Table 1. Transition-metal catalyzed silylboration and stannylboration in the presence of methanol[a]



Entry	Substrate R^1	R^2	Catalyst	Yield (%)[b]	Ratio[c] of I : II
$PhMe_2SiBEt_3Li$					
1	$^nC_{10}H_{21}$	H	CuCN	89	61 : 39
2			$CoCl_2(PPh_3)_2$	78	100 : 0
3	$PhCH_2OCH_2CH_2$	H	CuCN	91[d]	68 : 32
4			$CoCl_2(PPh_3)_2$	57	100 : 0
5	$^nC_5H_{11}$	$^nC_5H_{11}$	CuCN	73	——
6	$HOCH_2$	H	CuCN	95	100 : 0
7	$HOCH_2CH_2$	H	CuCN	95	78 : 22
8			$CoCl_2(PPh_3)_2$	96	100 : 0
9	$HOCH_2CH_2CH_2$	H	CuCN	96	66 : 34
10			$CoCl_2(PPh_3)_2$	81	100 : 0
11	$HOCH_2$	CH_3	CuCN	85	100 : 0
12	$HOCH_2CH_2$	CH_3	CuCN	97	91 : 9
13	$SiMe_3$	$^nC_5H_{11}$	CuCN	66	100 : 0
Bu_3SnBEt_3Li					
14	$PhCH_2OCH_2CH_2$	H	——	24[e]	100 : 0
15			CuCN	40[e]	65 : 35
16			$CoCl_2(PPh_3)_2$	58[e]	80 : 20
17	$HOCH_2CH_2$	H	$CoCl_2(PPh_3)_2$	47	100 : 0

a) Two mmol of $PhMe_2SiBEt_3Li$ (or Bu_3SnBEt_3Li) reagent, one mmol of acetylenic compound, 10 mol% of catalyst, and 10 mmol of methanol were employed. In the case of acetylenes having a hydroxyl group such as propargyl alcohol and 3-butyne-1-ol, the reaction proceeded without addition of methanol. However, 10 mmol of methanol was added to complete the reaction in a shorter period. b) Isolated yields unless otherwise noted. c) The ratios were determined by glpc and ^1H-NMR. d) See ref. 10. e) Glpc yields using $^nC_{28}H_{58}$ as an internal standard (OV-17 5% on Uniport HP 60-80 mesh, 2 m, 250°C).

References and notes

1. H. C. Brown, "Organic Synthesis via Boranes," John Wiley & Sons, New York, 1975; B. M. Mikhailov, Yu. N. Bubnov, "Organoboron Compounds in

Organic Synthesis," Harwood, New York, 1984; E. Negishi, "Organometallics in Organic Synthesis," Vol 1, John Wiley & Sons, New York, 1980; A. Suzuki, Topics in Current Chemistry, 112, 67 (1983).

2. a) W. Biffar and H. Nöth, *Angew. Chem.*, **92**, 65 (1980) or *Int. Ed. Engl.*, **19**, 58 (1980). b) idem, *Chem. Ber.*, **115**, 934 (1982).
3. Silylmetallation of acetylenic compounds has been reported. Y. Okuda, K. Wakamatsu, W. Tückmantel, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **26**, 4629 (1985) and references cited therein.
4. The reversible nature of the reaction of PhMe$_2$SiBEt$_3$Li with acetylenic compounds has been clearly demonstrated by the following result. Treatment of the reaction mixture derived from 4-benzyloxy-1-butyne and PhMe$_2$SiBEt$_3$Li with allyl bromide (5 equivalents) gave allyldimethylphenylsilane in 90% yield along with the recovered starting material (85%).
5. Moderate stability of silylborates to water has been reported. See ref. 2b. The use of acetic acid instead of methanol as a proton source resulted in the formation of a mixture containing the vinylsilane and starting material, 1-dodecyne (1:1).
6. Similar results have been reported in the reaction of stannylcopper and germylcopper reagents with acetylenic substrates. E. Piers and J. M. Chong, *J. Chem. Soc. Chem. Commun.* **1983**, 934; S. D. Cox and P. Wudl, *Organometallics*, **2**, 184 (1983); H. Oda, Y. Morizawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **25**, 3217 (1984).
7. We are grateful to Toyo Stauffer Chemical Co. for the gift of triethylborane.
8. δ = -28.5 has been reported for Me$_3$SiBMe$_3$Li. See ref. 2a.
9. The reaction proceeded easily even in the presence of a large excess of methanol (100 equivalents).
10. (E)-4-Benzyloxy-1-dimethylphenylsilyl-1-butene: Bp 100°C (bath temp, 0.045 Torr); IR (neat) 3080, 2970, 2870, 1623, 1434, 1255, 1115, 992, 820 cm^{-1}; NMR (CCl$_4$) δ0.30 (s, 6H), 2.39 (dt, *J* = 5.5 and 6.5 Hz, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 4.39 (s, 2H), 5.73 (d, *J* = 18.5 Hz, 1H), 6.07 (dt, *J* = 18.5 and 5.5 Hz, 1H), 7.1-7.45 (m, 10H). Found: C, 77.36; H, 8.37%. Calcd for C$_{19}$H$_{24}$OSi: C, 76.97; H, 8.16%. 2-Silyl isomer: IR (neat) 934 cm^{-1}; NMR (CCl$_4$) δ0.34 (s, 6H), 2.33 (t, *J* = 6.0 Hz, 2H), 3.30 (t, *J* = 6.0 Hz, 2H), 4.26 (s, 2H), 5.39 (m, 1H), 5.67 (m, 1H), 7.05-7.45 (m, 10H).
11. In contrast, silylboration did not proceed at all in the absence of transition-metal catalysts.
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