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NEW SYNTHESES OF VINYLSILANES AND ALLYLSILANES BY CROSS-COUPLING OF $(R_3Si)_3MnMgMe$ WITH ALKENYL AND ALLYLIC COMPOUNDS

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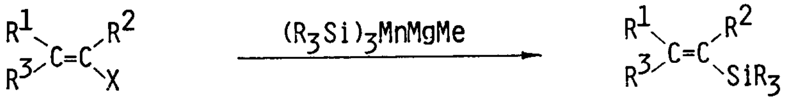
Abstract: The reaction of alkenyl halides, alkenyl sulfides, and enol phosphates with $(R_3Si)_3MnMgMe$ provides vinylsilanes in good yields. The method is also applicable to the allylsilane synthesis from allylic sulfides and ethers.

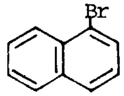
The reactions of organocuprate have been extensively studied and widely applied to organic synthesis.[1] In contrast, only little attention has been paid to the related reactions of triorganomanganese compounds.[2,3] In previous communication, we have demonstrated that silylmanganese reagent derived from $PhMe_2SiMgMe$ and Li_2MnCl_4 proved to be effective for the disilylation of acetylenes.[4] Here we wish to report further application of the reagent to the syntheses of vinylsilanes and allylsilanes starting from alkenyl halides (or alkenyl sulfides, or enol phosphates) and allylic sulfides (or allylic ethers).

An ethereal solution of MeMgI (1.1 M, 4.2 ml, 4.5 mmol) was added to a solution of $PhMe_2SiLi$ (0.68 M, 6.6 ml, 4.5 mmol) in THF under an argon atmosphere at 0°C. After stirring for 15 min, a THF solution of Li_2MnCl_4 (1.0 M, 1.5 ml, 1.5 mmol) was added and the resulting dark brown mixture was stirred for another 15 min. Then, a solution of (E)-1-iodo-1-dodecene (0.29 g, 1.0 mmol) in THF (2.0 ml) was added and the whole was stirred for 0.5 h at 0°C. The reaction mixture was diluted with hexane (25 ml) and treated with aq. NH_4Cl (20 drops). The mixture was filtered and precipitate was washed with ether. Combined filtrates were dried and concentrated in vacuo. Purification of the residue by preparative tlc on silica gel gave (E)-1-dimethylphenylsilyl-1-dodecene (0.22 g) in 72% yield. The representative results are summarized in Table 1.

Several comments are worth noting. (1) The reaction proceeded stereospecifically. Whereas (E)-1-iodo-1-dodecene gave (E)-dimethylphenylsilyl-1-dodecene exclusively, (Z)-1-iodo-1-dodecene provided (Z) vinylsilane preferentially. In the latter case, low reaction temperature such as -95°C was essential in order to obtain high stereospecificity (Entry 4) (2) Not

Table 1. Transformation of alkenyl halides, alkenyl sulfides, and enol phosphates into vinylsilanes with $(R_3Si)_3MnMgMe$[a]



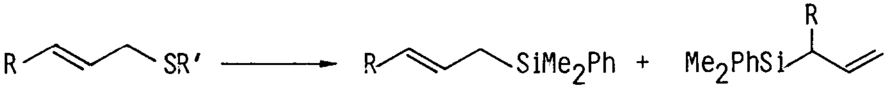
	Substrate				Condition		Product	
Entry	R^1	R^2	R^3	X	Temp(°C)	Time(h)	Y(%)[b]	E/Z
$(PhMe_2Si)_3MnMgMe$								
1	Me(H)	H	H(Me)	Br[c]	0	3	100	47/53
2	$^nC_{10}H_{21}$	H	H	I	0	0.5	72	100/0
3	H	H	$^nC_{10}H_{21}$	I	0	0.5	73	20/80
4	H	H	$^nC_{10}H_{21}$	I	-95	1.3	40[d]	0/100
5	H	H	Ph	Br	25	1	70	39/61
6	H	H	Ph	Br	-78	3	50	0/100
7	Me	H	Me	Br	0	0.5	70	——
8	$^nC_{10}H_{21}$	H	Me	I	0	2	75[e]	100/0
9	$^nC_5H_{11}$	$^nC_5H_{11}$	Me	I	0	2	47[f,g]	80/20
10	$-(CH_2)_4-$		H	Br	0	2	93	——
11					0	2	65	——
12	Ph	H	H	SMe	0	1	70	100/0
13	$-(CH_2)_4-$		H	SMe	0	1	75	——
14	H	$^nC_6H_{13}$	H	$OP(O)(OPh)_2$	25	5	74	——
15	$-(CH_2)_4-$		H	$OP(O)(OEt)_2$	0	1	66	——
16	H	$^nC_4H_9$	H	OSO_2CF_3	0	1	99	——
$(Me_3Si)_3MnMgMe$								
17	H	$^nC_{10}H_{21}$	H	I	0	3	100	——
18	$^nC_{10}H_{21}$	H	H	I	-95	2	100	30/70
19	$-(CH_2)_6-$		H	SPh	0	3	89	——

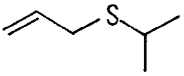
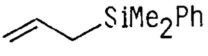
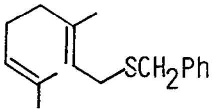
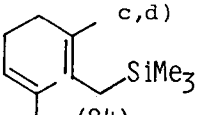
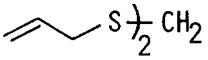
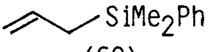
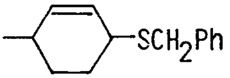
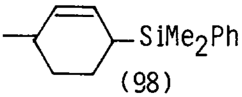
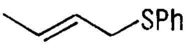
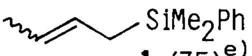
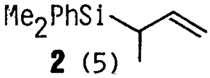
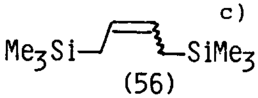
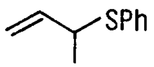
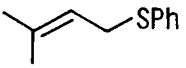
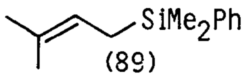
a) Manganese reagent (1.5 mmol) and substrate (1.0 mmol) were employed. b) Isolated yields. c) Commercially available 1-bromo-1-propene (Aldrich Chemical Co.) was used (E/Z = 40/60). d) Starting material was recovered (30%). e) 2-Methyl-1-dodecene was obtained as byproduct (5% yield). f) See ref. 5. g) (Z)-6-Methyl-6-dodecene was also obtained (25% yield).

only alkenyl halides[6] but also alkenyl sulfides and enol phosphates were easily converted into the corresponding vinylsilanes. Vinyl ether such as 1-methoxycyclohexene was reluctant to react with manganese reagents and provided only a trace of the desired vinylsilane (<5%). (3) The use of MeMgI was essential for the reaction. The reaction of diethylcyclohexenylphosphate with $(R_3Si)_3MnLi$ gave cyclohexanone upon workup because the reagent caused nucleophilic attack on phosphorus atom. (4) The amount of Li_2MnCl_4 could be reduced to a catalytic amount. For instance, treatment of diethylcyclohexenylphosphate (0.5 mmol) with $PhMe_2SiMgMe$ (1.5 mmol) in the presence of a catalytic amount of Li_2MnCl_4 (0.1 mmol) gave the desired vinylsilane in 66% yield.

Allylic sulfides also smoothly coupled with $(PhMe_2Si)_3MnMgMe$ to give the corresponding allylic silanes in good yields.[7] The results are summarized in Table 2. The reaction proceeded with high regioselectivity.[8]

Table 2. Allylsilane synthesis by cross coupling of allylic sulfides and ethers with $(PhMe_2Si)_3MnMgMe$



Sulfide	Product Yield(%)	Sulfide	Product Yield(%)
	 (91)		 (84) c,d)
	 (60)		 (98)
	 **1** (75)[e)]  **2** (5)		 (56) c)
	**1** (88)[f] **2** (2)	 R" = CH_2Ph R" = $SiMe_2{}^tBu$	 **1** (65)[g)] **2** (5) **1** (71)[h)] **2** (2)
	 (89)		

a) Reactions were performed at 0°C for 30 min. Two mmol of the reagent and one mmol of substrate were employed. b) Isolated yields. c) $(Me_3Si)_3MnMgMe$ was used instead of $(PhMe_2Si)_3MnMgMe$. d) Reaction mixture was stirred for 15 h. e) E/Z = 5/1. f) E/Z = 2/1. g) E/Z = 20/1. h) E/Z = 20/1.

Both (E)-1-phenylthio-2-butene and 3-phenylthio-1-butene gave 1-dimethylphenylsilyl-2-butene (**1**) as a main product along with the regio isomer, 3-dimethylphenylsilyl-1-butene (**2**). Allylic ethers[9] such as 1-benzyloxy-2-butene and 1-t-butyldimethylsiloxy-2-butene easily reacted with manganese reagent to give the corresponding allylsilanes.

References and Notes

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2. J. F. Normant, Organocopper and Organomanganous reagent in "Modern Synthetic Methods", Vol. 3, R. Scheffold ed., Otto Salle Verlag GmbH & Co., Frankfurt an Main, p. 139 (1983).
3. Cross coupling reaction between alkenyl halides and Me_3MnLi has been reported. E. J. Corey and G. H. Posner, Tetrahedron Lett., **1970**, 515.
4. J. Hibino, S. Nakatsukasa, K. Fugami, S. Matsubara, K. Oshima, and H. Nozaki, J. Am. Chem. Soc., **107**, 6416 (1985).
5. Bp. 133°C (0.1 Torr, bath temp); IR (neat) 2954, 2925, 2854, 2085, 1610, 1466, 1047, 1110, 830, 770 cm^{-1}; NMR ($CDCl_3$) δ 0.30 (s, 6H), 0.75-1.00 (m, 6H), 1.10-1.45 (m, 12H), 1.61 (s, 2.4H), 1.73 (s, 0.6H), 2.00-2.20 (m, 4H), 7.25-7.40 (m, 3H), 7.45-7.60 (m, 2H). Found: C, 79.62; H, 11.60%. Calcd for $C_{21}H_{36}Si$: C, 79.67; H, 11.46%.
6. Transformation of alkenyl halides into vinylsilanes by Wurtz-type coupling has been reported. T. H. Chan, A. Baldassarre, D. Massuda, Synthesis, **1976**, 801; G. Nagendrappa, ibid., **1980**, 704; I. Fleming and A. Pearce, J. Chem. Soc. Perkin I, **1980**, 2485.
7. Cross coupling reactions between allylic sulfides and Grignard reagents in the presence of transition-metal catalyst have been reported. Y. Gendreau, J. F. Normant, and J. Villieras, J. Organomet. Chem., **142**, 1 (1977); P. Barsanti, V. Calò, L. Lopez, G. Marchese, F. Naso, and G. Pesce, J. Chem. Soc. Chem. Commun., **1978**, 1085; H. Okamura and H. Takei, Tetrahedron Lett., **1979**, 3425.
8. Transformation of allylic phosphates into allylsilanes with $PhMe_2SiAlEt_2$ has been reported. In the case of unsymmetric allylic phosphates, mixtures of unrearranged products (S_N2) and rearranged products (S_N2') were obtained. Y. Okuda, M. Sato, K. Oshima, and H. Nozaki, Tetrahedron Lett., **24**, 2015 (1983).
9. Allylic halides also provided allylsilanes in good yields. Treatment of crotyl bromide with $(PhMe_2Si)_3MnMgMe$ gave a mixture of crotyl silane **1** (80%) and isomer **2** (2%).

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