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STEREO- AND REGIOSELECTIVE ROUTES TO ALLYLIC SILANES[1]

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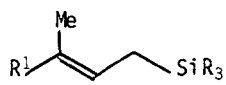
SUMMARY: The Ni- or Pd-catalyzed reaction of alkenyl iodides with Me_3SiCH_2MgCl provides various types of allyltrimethylsilanes in excellent yields in a highly stereo- and regioselective manner, while the Zr-catalyzed carboalumination of $Me_3SiCH_2C{\equiv}CH$ followed by replacement of Al with carbon groups by known reactions produces allylsilanes represented by 2.

Recently, allylsilanes have emerged as useful intermediates for organic synthesis.[2] Their usefulness, however, has been limited by the lack of selective and convenient methods for their synthesis. Although the reaction of allylmagnesium halides with silyl electrophiles,[3] e.g., Me_3SiCl, is versatile, the preparation of the required allylmagnesium halides is plagued with relatively low yields as well as stereo- and regioscrambling of the allyl group.

In connection with our study of the Si-directed polyene cyclization, it became desirable to develop selective and convenient routes to allylsilanes, especially those represented by 1 and 2.



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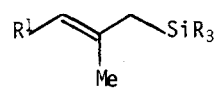
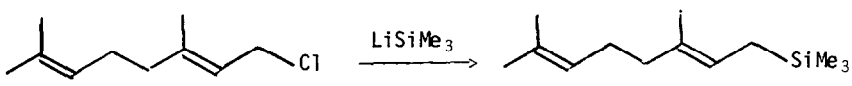


2

We specifically hoped to develop stereo- and regioselective procedures involving the Zr-catalyzed carboalumination[4] of alkynes.

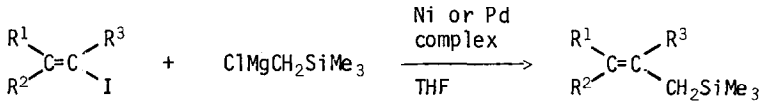
One obvious approach which has remained relatively untested[5] involves the reaction of allylic halides with silanions. We therefore prepared $LiSiMe_3$ by a literature procedure[6] and reacted it with isoprenyl and geranyl chlorides in THF (-78°C to room temperature). The desired isoprenyltrimethylsilane and geranyltrimethylsilane (3) were obtained in 82 and 81% yields, respectively (eq 1). As expected, the stereoisomeric purity of 3 is ≥98% by GLC and ^{13}C NMR criteria. Although the full scope of this method is yet to be examined, the results described above indicate that it is distinctly superior to the conventional method involving the reaction of allylmagnesium halides with silyl electrophiles[3] in terms of both product yield and selectivity.



(1)

3 (81%, ≥98% *E*)

The two methods described above involve the formation of the C-Si bond in the allylsilane forming step. As alternate routes to allylsilanes we then sought procedures involving formation of C-C single bonds to the alkenyl carbons. We have indeed found that the reaction of alkenyl iodides, readily available *via* hydrometallation[7] and carbometallation[8] with trimethylsilylmethylmagnesium chloride[9] in the presence of a catalytic amount, e.g., 5 mol %, of a Ni-phosphine or Pd-phosphine complex, e.g., $Pd(PPh_3)_4$, provides the desired allylsilanes in excellent yields (eq 2).



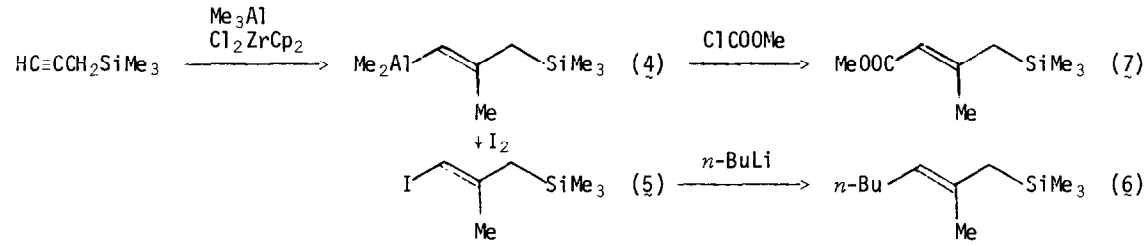
(2)

Since there is no reaction in the absence of the Ni or Pd catalyst, the reaction is catalytic in Ni or Pd. As shown in the Table (*E*)- and (*Z*)-γ-monosubstituted and γ,γ-disubstituted allylsilanes have been obtained in a highly stereoselective manner (≥98%). Although the use of $Pd(PPh_3)_4$ resulted in somewhat higher product yields than that of $Ni(PPh_3)_4$, we judge that both are of comparable efficiency in typical cases. Treatment of the Grignard reagent with $ZnCl_2$ prior to cross coupling does not improve the yield. Our attempts to react directly alkenylalanes obtainable *via* hydroalumination[7] or carboalumination[4] of alkynes with Me_3SiCH_2Cl or Me_3SiCH_2I in the presence of a Ni- or Pd-phosphine complex to form allylsilanes have been unsuccessful.

The following procedure for the synthesis of (*E*)-3-methyl-2-heptenyltrimethylsilane from 1-hexyne is representative. (*E*)-1-Iodo-2-methyl-1-hexene was prepared in 92% yield by carboalumination-iodination of 1-hexyne with Me_3Al-Cl_2ZrCp_2 followed by treatment wit I_2 in THF, as described previously.[8a] Trimethylsilylmethylmagnesium chloride was prepared in quantitative yield by the addition of 12.27 g (100 mmol) of Me_3SiCH_2Cl to 2.92 g (120 mmol) of magnesium covered with 50 ml of diethyl ether at room temperature. To 5.77 g (5 mmol) of $Pd(PPh_3)_4$ in 50 ml of THF were added sequentially the Grignard reagent prepared above and 20.2 g (90 mmol) of (*E*)-1-iodo-2-methyl-1-hexene at 0°C. After stirring the reaction mixture for 12 hr at room temperature, it was quenched with 3 *N* HCl and extracted with hexane. The organic layer was washed with aq $NaHCO_3$ followed by water, and was dried over $MgSO_4$. Evaporation of volatile compounds gave 14.1 g (85% yield) of >95% pure (GLC) (*E*)-3-methyl-2-heptenyltrimethylsilane (≥98% *E*), which was purified by short-path column chromatography (silica gel, hexane): $n^{23}D$ 1.4405; ^1H NMR ($CDCl_3$, TMS) δ 0.00 (s, 9H), 0.90 (t, J = 7 Hz, 3H), 1.1-1.5 (m, 6H), 1.65 (s, 3H), 2.00 (t, J = 7 Hz, 2H), and 5.19 (t, J = 7 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ -1.69, 14.01, 15.73, 18.62, 22.37, 30.66, 39.73, 119.97, and 132.71 ppm.
High resolution MS Calcd for $C_{11}H_{24}Si$: 184.165. Found: 184.165.

The preparation of β,γ-disubstituted allylsilanes, e.g., 2, by the above-described method requires alkenyl iodides derived from internal alkynes. Since hydrometallation reactions[7] of internal alkynes are generally not regioselective, such alkenyl iodides are not readily available as isomerically pure compounds. We therefore undertook to develop a procedure involving the use

of trimethylsilylmethyl substituted alkenylalanes (4) or the corresponding alkenyl iodides (5) as key intermediates. We were pleased to find that the Zr-catalyzed carboalumination[4] of 3-trimethylsilylpropyne[10] proceeded to produce, after iodinolysis,[8a] (*E*)-1-iodo-2-methyl-3-trimethylsilylpropene (5). To a solution of Me_3Al (1.44 g, 20 mmol) and Cl_2ZrCp_2 (0.29 g, 1 mmol) in 1,2-dichloroethane was added at 0°C 3-trimethylsilyl-1-propyne (1.11 g, 10 mmol). After stirring the reaction mixture for 2 hr at room temperature, it was treated sequentially with I_2 (3.05 g, 12 mmol) dissolved in 20 ml of THF at -30°C, ice water, and 3 *N* HCl, and extracted with hexane. The organic extract was washed with water and aqueous $NaHCO_3$, dried over $MgSO_4$, concentrated, and flash chromatographed (silica gel, hexane) to give 1.60 g (63%) of 5: $n^{23}D$ 1.5750; ^1H NMR ($CDCl_3$, TMS) δ 0.00 (s, 9H), 1.79 (s, 3H), 1.81 (s, 2H), and 5.54 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ -1.41, 26.38, 30.82, 69.56, and 145.56 ppm; IR (neat) 1600 (w) cm^{-1}. Conversion of 5 into γ-carbon substituted derivatives 2 can, in principle, be achieved by various known carbon-carbon bond forming reactions of alkenyl iodides, such as their reactions with organolithiums,[11] organocuprates,[12] Grignard reagents in the presence of a Ni-phosphine complex,[13] and organozincs in the presence of Pd-phosphine complex.[14] For example, treatment of 5 with *n*-BuLi in THF (-50°C, 3 hr) gives 6 in 78% isolated yield (87% by GLC): ^1H NMR ($CDCl_3$, TMS) δ 0.00 (s, 9H), 0.90 (t, *J* = 7 Hz, 3H), 1.1-1.4 (m, 4H), 1.46 (s, 2H), 1.59 (s, 3H), 1.7-2.15 (m, 2H), and 4.95 (t, *J* = 7 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ -1.21, 14.05, 18.60, 22.46, 28.02, 29.98, 32.57, 123.04, and 132.23 ppm. Its ^1H and ^{13}C NMR spectra indicate that it is stereochemically ≥98% pure. Alternatively, the carbometallated product 4 can be treated with various carbon electrophiles, such as ClCOOMe,[15] CO_2,[15] paraformaldehyde,[15] $ClCH_2OMe$,[15] and epoxides,[16] either directly or after treating 4 with one equivalent of *n*-BuLi. For example, the reaction of 4 with ClCOOMe produces 7, which is stereochemically ≥98% pure, in 57% isolated yield: ^1H NMR ($CDCl_3$, TMS) δ 0.07 (s, 9H), 1.74 (s, 2H), 2.17 (s, 3H), 3.65 (s, 3H), and 5.48 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ -1.35, 21.45, 33.60, 50.25, 112.93, 160.16, and 166.85 ppm; IR (neat) 1710(s), 1630(s), 1140(s), 850(s) cm^{-1}.



We are currently applying these procedures to the preparation of allylically Si-substituted terpenoids.

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Table. Pd-Catalyzed Reaction of Alkenyl Iodide with Trimethylsilylmethylmagnesium Chloride or Its Zinc Analogue[a]

R^1	R^2	M^1 of $Me_3SiCH_2M^1Cl$	M^2 of $M^2(PPh_3)_4$	Yield[b] (%) of Allylsilane	^1H NMR Chemical Shift (δ, ppm)	^{13}C NMR Chemical Shift (δ, ppm)
n-Hex	Me	Zn	Pd	80 (83)	0.0, 0.9, 1.1-1.4,	-1.66, 14.15, 15.76, 18.64,
"	"	Mg	"	– (85)	1.42, 1.53, 1.98,	22.80, 28.36, 29.04, 31.94,
"	"	Zn	Ni	– (47)	5.18	40.03, 120.01, 132.75
"	"	Mg	"	– (74)		
n-Bu	"	Zn	Pd	– (74)	See text.	See text.
"	"	Mg	"	85		
n-Hex	H	"	"	70 (84)	0.0, 0.9, 1.3,	-1.96, 14.14, 22.69, 22.79,
"	"	"	Ni	– (76)	1.42, 1.8-2.2,	28.94, 30.12, 31.92, 32.91,
					5.1-5.6	125.96, 129.18
H	*n*-Pr	"	Pd	– (84)	0.0, 0.9, 1.2-1.4,	-1.54, 14.15, 18.66, 23.20,
"	"	"	Ni	78 (89)	1.5, 1.8-2.1,	29.45, 125.64, 127.78
					5.1-5.5	

[a] The reaction was carried out in diethyl ether-THF at room temperature using 5 mol % of $Pd(PPh_3)_4$ or $Ni(PPh_3)_4$ as a catalyst. [b] Isolated yield. The numbers in parentheses are GLC yields. All isolated products have been identified by ^1H and ^{13}C NMR, IR, and high resolution MS. In each case the stereoisomeric purity of the product is $\geq$98%.

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