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SYNTHESIS OF FUNCTIONALIZED ALLYLSILANES VIA PALLADIUM-CATALYZED CROSS-COUPLING OF 2-STANNYL-3-SILYLPROPENE WITH ORGANIC HALIDES.

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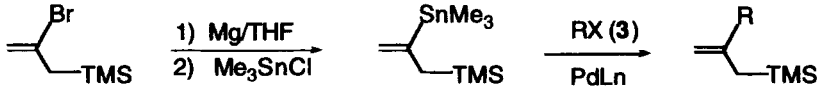
Summary: *Allylsilanes bearing the various functionalities were prepared from the palladium-catalyzed cross-coupling reactions of 2-trimethylstannyl-3-trimethylsilylpropene with acid chlorides and with aryl halides.*

Allylsilanes have emerged as highly useful intermediates in organic synthesis.[1] Transition metal-catalyzed cross-coupling reactions of organo-magnesium, -lithium or -zinc compounds with silyl enol ethers, enol phosphates, vinyl or aryl halides provide various types of allylsilanes.[2] However, these methods are not suitable for the preparation of allylsilanes carrying reactive functionalities.[3] Palladium-catalyzed cross-coupling reactions of organotins with electrophiles leading to new carbon-carbon bonds are well documented.[4] The advantage of this type of reaction is that a wide variety of functional groups on either partner, including ester, nitrile, alcohol and even aldehyde can tolerate.

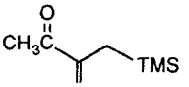
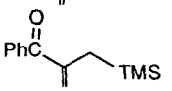
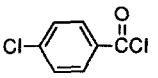
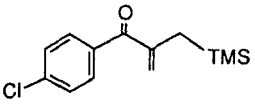
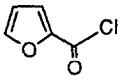
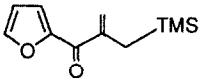
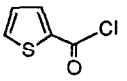
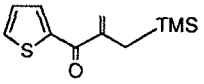
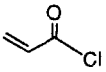
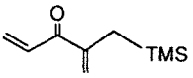
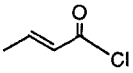
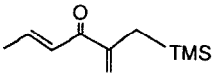
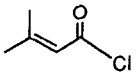
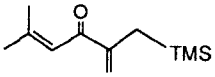
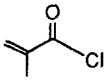
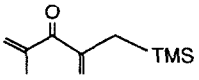
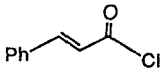
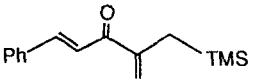
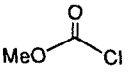
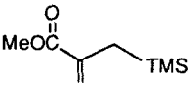
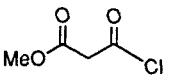
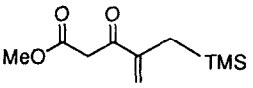
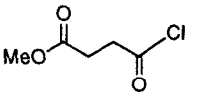
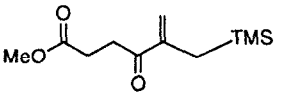
We found that the palladium-catalyzed cross-coupling of 2-trimethylstannyl-3-trimethylsilylpropene (**2**) with organic halides is a new and versatile method for the synthesis of the variously functionalized allylsilanes. Thus, when 3-trimethylsilyl-2-propenylmagnesium bromide generated from 2-bromoallyltrimethylsilane(1)[5] in tetrahydrofuran was allowed to react with trimethyltin chloride, **2** was produced in 70% yield.[6] **2** underwent smooth coupling reactions with various acid chlorides to produce allylsilanes, **4**.

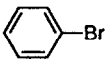
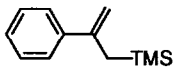
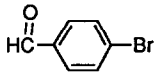
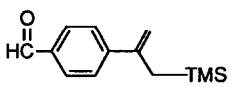
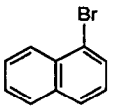
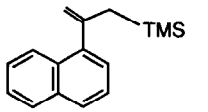
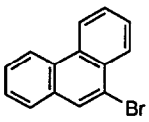
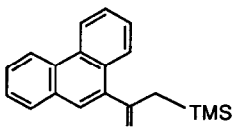
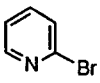
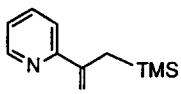


1 **2** **4**

The coupling of acetyl chloride (**3a**) with **2** illustrates a typical procedure. **3a** (160 mg, 2.0 mmol), chloroform (2 mL), **2** (554 mg, 2.0 mmol) and $PhCH_2Pd(PPh_3)_2Cl$ (30.4 mg, 0.04 mmol) were placed in a flask mounted with a calcium chloride tube. The yellow solution was heated to 65 °C with stirring until blackening occurred (12h). After the mixture was cooled to room temperature, 15 mL of dichloromethane and 10 mL aq. NH_4Cl solution were added. The organic layer was separated and the water layer was washed with dichloromethane (10 mL). The combined extracts

Table 1. Reaction of Electrophiles **3** with Tin Reagent **2** Catalyzed by Palladium Complex.

Entry	Electrophile **3**	Reaction Conditions [a] (day)	Product [b] **4**	Yield [c] %
a		A (0.5)		81
b		A (1)		73
c		A (1)		69
d		A (2)		67
e		A (2)		58
f		A (1)		75
g		A (1)		89
h		A (1)		74
i		A (1)		75
j		A (1)		73
k		A (2)		49
l		A (1)		38
m		A (2)		60

Entry	Elecrophile 3	Reaction Conditions[a](day)	Product[b] 4	Yield[c] %
n		A (1)		68
o		A (1)		40
p		B (2)		45
q		B (3)		35
r		B (2)		44

[a] Procedure A: reaction with equimolar amount of the organic halide and **2** in chloroform at 65 °C in the presence of 1-2 mol % $PhCH_2Pd(PPh_3)_2Cl$ (**5**). Procedure B: reaction of an aryl halide with 1.2 equivalents of **2** and **5** (1 mol %) in HMPA at 65 °C. [b]The products were fully characterized by ^1H, ^{13}C NMR and MS spectra.[7] [c] Isolated yields.

were dried (Na_2SO_4) and concentrated. Column chromatography on silica gel (hexane:ether = 10:1) afforded 252 mg of allylsilane **4a** (81%). Following a similar procedure, 2-acylallylsilanes were prepared in good yields from both aromatic-(**3b-c**) and heterocyclic-(**3d-e**) acid chlorides. α,β-Unsaturated acid chlorides (**3f-j**) with **2** also gave α-(trimethylsilylmethyl)divinyl ketones in good yields. No conjugate addition product was observed. Methyl chloroformate (**3k**), methyl malonyl chloride (**3l**) and methyl succinyl chloride (**3m**) also produced the corresponding allylsilanes (**4k-m**) in moderate yields.

2 also underwent palladium-catalyzed coupling reactions with aromatic halides to afford 2-arylallylsilanes (entries n-q). For example, the reactions of bromobenzene (**3n**) and *p*-bromobenzaldehyde (**3o**) with **2** in chloroform under the same conditions as described above gave **4n** and **4o**, respectively. The yields were not greatly improved even when the reactions were carried out in HMPA. 1-Bromonaphthalene (**3p**) and 2-bromopyridine (**3q**) gave poor yields (<5%) of allylsilanes in chloroform, but the yields were improved to 40-50% when the reactions were performed in HMPA.

The manipulation and work up of the reactions are very simple. The present reaction provides a versatile synthesis for a variety of functionalized allylsilanes.

We are continuing to explore the synthetic applications of the obtained allylsilanes including Nazarov cyclization of α-(trimethylsilylmethyl)divinyl ketones.

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References and Notes

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2. For recent review articles, see: Sarkar, T. K. *Synthesis*, **1990**, 969; 1101.

3. Pd(0) catalyzed cross-coupling of vinyl triflates with tris(trimethylsilylmethyl)aluminum provide certain functionalized allylsilanes. Saulnier, M. G.; Kadow, J. F.; Tun, M. M.; Langley, D. R.; Vyas, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 8320.

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5. Nishiyama, H.; Yokoyama, H.; Narimatsu, S.; Itoh, K. *Tetrahedron Lett.* **1982**, *23*, 1267.

6. **2** was prepared from the reaction of the anion generated by lithiodestannylation of 2,3-bis-(trimethylstannyl)propene with methyllithum and trimethylsilyl chloride. Mitchell, T. N.; Kwetkat, K.; Rutschow, D.; Schneider, D. *Tetrahedron*, **1989**, *45*, 969.

7. Spectral data for the selected allylsilanes are given below.
4a: ^{1}H-NMR ($CDCl_3$) δ -0.06 (s, 9H), 1.77 (s, 2H), 2.31 (s, 3H), 5.57 (s, 1H) 5.83 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ -1.17, 20.72, 25.45, 122.1, 147.3, 199.5; MS m/z 155 (M^+-1, 2), 141 (M^+-CH_3, 100), 73 (40%). **4c**: ^{1}H-NMR δ 0.03 (s, 9H), 2.01 (s, 2H), 5.47 (s, 1H), 5.72 (s, 1H), 7.3 - 7.7 (m, 4H); ^{13}C-NMR δ 1.53, 22.7, 124.2, 128.4, 130.8, 136.1, 138.2, 146.1, 196.7; MS m/z 251 (M^+-Cl, 5), 237 (8), 217 (24), 202 (7), 163 (9), 139 (7), 128 (15), 111 (13), 93 (7), 74 (100%). **4d:** ^{1}H-NMR δ 0.00 (s, 9H), 1.97 (s, 2H), 5.58 (s, 1H), 5.81 (s, 1H), 6.52 (dd, 1H, J = 3.7, 2.0 Hz), 7.11 (d, 1H, J = 3.7 Hz), 7.64 (d, 1H, J = 2.0 Hz); ^{13}C-NMR δ -1.67, 22.8, 111.7, 119.5, 121.4, 146.0, 146.8, 151.7, 184.2; MS m/z 208 (M^+, 5), 207 (12), 193 (70), 179 (12),165 (12), 125 (20), 95 (27), 91 (26), 75 (22), 74 (100), 73 (62), 69 (10), 59 (12%). **4f**: ^{1}H-NMR δ -0.02 (s, 1H), 1.88 (s, 1H), 5.63 (s, 1H), 5.74 (dd, 1H, J = 10.5, 1.8 Hz), 5,84 (s, 1H), 6.25 (dd, 1H, J = 16.8, 1.8 Hz), 6.92 (dd, 1H, J = 16.8, 10.5 Hz); ^{13}C-NMR δ -1.70, 21.55, 121.9, 128.3, 131.7,147.3, 192.0; MS m/z 168 (M^+, 14), 167 (44), 153 (78), 147 (21), 140 (24), 73 (100%). **4j**: ^{1}H-NMR δ 0.03 (s, 9H), 1.96 (s, 2H), 5.66 (s, 1H), 5.94 (s, 1H), 7.33 (d, 1H, J = 15.6 Hz), 7.4 - 7.6 (m, 5H), 7.66 (d, 1H, J = 15.6 Hz); ^{13}C-NMR δ -0.61, 21.89, 120.4, 121.5, 128.2, 128.9, 130.1, 135.0, 143.2, 148.2, 191.6; MS m/z 244 (M^+, 68), 243 (46), 229 (31), 155 (22), 131 (13), 103 (17), 73 (100%). **4m**: ^{1}H-NMR δ -0.09 (s, 9H), 1.76 (s, 2H), 2.57 (t, 2H, J = 6.8 Hz), 3.00 (t, 2H, J = 6.8 Hz), 3.63 (s, 3H), 5.56 (s, 1H), 5.87 (s, 1H); ^{13}C-NMR δ -1.78, 20.98, 28.21, 32.07, 51.66, 121.4, 146.5, 173.3, 199.2 ; MS m/z 228 (M^+,1), 213 (24), 197 (15), 169 (32), 153 (99), 73 (100), 59 (28%). **4o**: ^{1}H-NMR δ -0.08 (s, 9H), 2.06 (s, 2H), 5.01 (s, 1H), 5.26 (s, 1H), 7.54 -7.86 (m, 4H), 10.00 (s, 1H); ^{13}C-NMR δ -1.28, 25.94, 112.6, 126.7, 129.7, 135.2, 145.7, 149.0, 191.7; MS m/z 218 (M^+, 69), 203 (19), 115 (20), 91 (18), 73 (100%). **4r**: ^{1}H-NMR δ -0.09 (s, 9H), 2.21 (s, 2H), 5.08 (s, 1H), 5.53 (s, 1H), 7.01 - 7.14 (m, 1H), 7.46 - 7.50 (m, 1H), 7.58 - 7.63 (m, 1 H), 8.54 - 8.56 (m, 1 H); ^{13}C-NMR δ -1.53, 24.09, 112.3, 120.3, 121.8, 138.0, 146.6, 148.6, 158.5; MS m/z 191 (M^+, 70), 176 (100), 162 (29), 146 (12), 118 (16), 117 (21), 73 (60%).

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