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Cross-coupling reaction: stereoselective synthesis of (*E*)-aryl or heteroarylvinylgermanes

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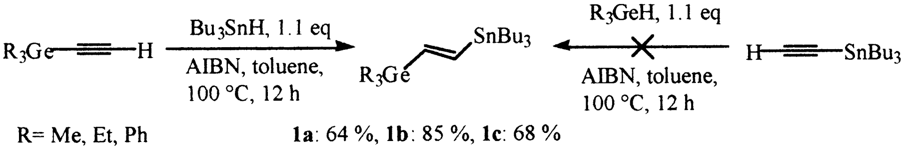
Abstract

(*E*)-Aryl or heteroarylvinylgermanes are obtained by Stille reactions using (*E*)-1-tributylstannyl-2-trialkyl (or triphenyl) germylethylenes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: organogermanium and compounds; palladium catalyst; coupling reactions.

The synthetic utilities of organogermyl compounds have not been fully studied, but organogermyl species have been recognized as important compounds for organic syntheses.[1,2] In this field, the synthesis of vinylgermanes is becoming increasingly used and has demonstrated a new focus for their synthesis.[3] They were obtained recently by olefination of carbonyl compounds with triethylgermyl-substituted bis(bromozinciomethane) in the presence of $TiCl_2$ or by dehydrogenative germylation of styrene catalyzed by ruthenium complexes.[4]

Similarly, vinyltin reagents have proved to be efficient tools for the transfer of vinyl unit with a high tolerance for numerous functions both on the substrate and on the reagent.[5] For this purpose, we propose new vinyltin compounds bearing a germyl group at the β-position. The organotin precursors required are easily obtained by hydrostannation of alkynylgermanes under the experimental conditions used for the synthesis of (*E*)-1,2-bis(tributylstannyl)ethylene.[6]



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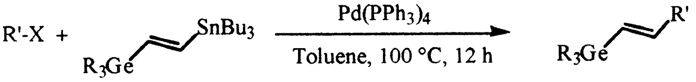
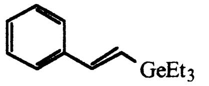
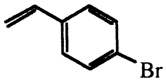
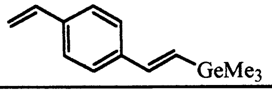
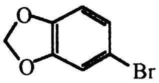
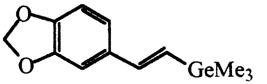
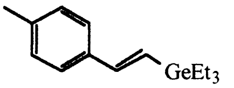
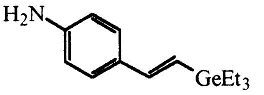
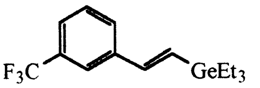
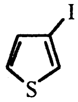
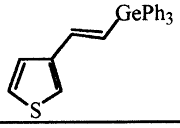
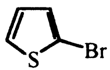
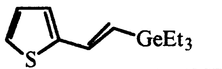
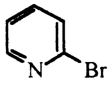
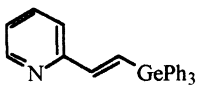
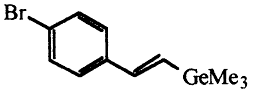
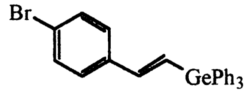
Good yields of **1a**, **1b**, **1c** are obtained and the *E* isomers are obtained stereospecifically. It should be noted that the addition of the germanium hydride on tributyltinacetylene failed under the same experimental conditions and the reactants were recovered.

The reactivity of these new compounds **1a**, **1b** or **1c** was examined in the situation of cross-coupling with organic halides under catalysis with palladium complexes.[7]



The results are presented in Table 1.[8]

Table 1

R'-X	R	Product	Yield	N°
Ph-I	Et		69	**2a**
	Me		63	**2b**
	Me		69	**2c**
p-Me-Ph-Br	Et		85	**2d**
p-NH2-Ph-I	Et		35	**2e**
m-CF3-Ph-Br	Et		56	**2f**
	Ph		61	**2g**
	Et		59	**2h**
	Ph		71	**2i**
p-Br-Ph-Br	Me		78	**2j**
p-Br-Ph-Br	Ph		81	**2k**

According to the results reported in Table 1, the substitution reaction appears to have a general character with complete control of the configuration, leading to (*E*)-aryl or heteroaryl vinylgermanes. It should also be noted that no competition occurred with the possible transfer of a vinylstannyl unit; this was identical when we used the (*E)*-1-tributylstannyl-2-trimethylsilylethylene system and only the trimethylsilylvinyl unit is transferred.[9]

These results demonstrate the efficiency of (*E*)-1-tributylstannyl-2-trialkyl (or triphenyl) germylethylenes to obtain (*E*)-aryl or heteroarylvinylgermanes and more generally to transfer the β-vinylgermyl synthon onto miscellaneous substrates. The value of these new organogermyl compounds as reaction intermediates is now being studied.

Acknowledgements

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8. *Typical procedure*: preparation of **2d**: 0.04 g (0.03 equiv.) of tetrakistriphenylphosphine(0) is added to a toluene solution (15 mL) of *p*-bromotoluene (1.15 mmol, 0.20 g) and, after stirring for 15 min, 1.25 mmol (0.595 g) of (*E*)-1-tributylstannyl-2-triethylgermylethylene diluted in 10 mL of toluene are added dropwise. The mixture is stirred overnight at 100°C. After cooling, the reaction mixture is filtered through a Celite path and treated with a 1 M solution of potassium fluoride to eliminate the tributyltin bromide formed. The aqueous layer is extracted with diethyl ether. The organic layer is washed with brine and dried over $MgSO_4$. After evaporation of the solvents, (*E*)-1-triethylgermyl-2-(*p*-tolyl)ethylene **2d** is purified by column chromatography on silica gel (petroleum ether/triethylamine: 98/2).
   ^1H NMR δ ppm (CD_2Cl_2, 200 MHz): 0.8–1.2 (15H, m), 2.34 (3H, s), 6.55 (1H, d, $J=19$ Hz), 6.82 (1H, d, $J=19$ Hz), 7.15 (2H, d, $J=8.5$ Hz), 7.36 (2H, d, $J=8.5$ Hz); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 4.7, 9.1, 21, 126.3, 126.4, 129.5, 136.1, 137.9, 143.6; MS (70 eV) m/z (^{74}Ge): 278 (M, 9), 249 (100), 235 (24), 221 (26), 191 (14), 165 (15), 105 (12).

2a: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 0.8–1.16 (15H, m), 6.65 (1H, d, $J=19$ Hz), 6.88 (1H, d, $J=19$ Hz), 7.24–7.48 (5H, m); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 4.7, 9.1, 126.4, 128, 128.2, 129, 138.9, 143.7; MS (70 eV) m/z (^{74}Ge): 264 (M, 10), 235 (100), 207 (38), 177 (24), 151 (23), 130 (10). **2b**: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 0.34 (9H, s), 6.71 (1H, d, $J=19$ Hz), 6.92 (1H, d, $J=19$ Hz), 7.33 (2H, bd), 7.47 (2H, bd); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): −1.7, 121.7, 128.1, 131.6, 132.9, 137.7, 141.1; MS (70 eV) m/z (^{74}Ge): 302 (13), 300 (M, 9), 287 (54), 285 (100), 191 (16), 115 (29), 105 (49), 89 (24), 78 (15). **2c**: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 6.95 (1H, d, $J=19$ Hz), 7.1 (1H, d, $J=19$ Hz), 7.4–7.6 (19H, m); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 122.4, 125.7, 128.7, 128.9, 129.6, 132.0, 135.4, 136.5, 137.2, 145.8; MS (70 eV) m/z (^{74}Ge): 488 M, 12), 486 (M, 15), 407 (13), 329 (10), 305 (20), 256 (14), 228 (100), 178 (45), 151 (59), 102 (11). **2e**: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 0.8–1.2 (15H, m), 3.76 (2H, bs), 6.34 (1H, d, $J=19$ Hz), 6.63 (2H, d, $J=8.5$ Hz), 6.73 (1H, d, $J=19$ Hz), 7.22 (2H, d, $J=8.5$ Hz); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 4.7, 9.1, 115.0, 122.7, 129.2, 129.5, 143.4, 146.9; MS (70 eV) m/z (^{74}Ge): 279 (M, 15), 250 (100), 222 (52), 192 (29), 166 (46), 146 (15), 131 (22), 117 (22), 103 (28), 97 (27). **2f**: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 0.8–1.1 (15H, m), 6.75 (1H, d, $J=19$ Hz), 6.89 (1H, d, $J=19$ Hz), 7.4–7.7 (4Har, m); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 4.7, 9.1, 124.3, 124.7 ($J=272$ Hz), 127.5, 129.4, 129.8, 131.2, 131.3, 139.6, 142.1; ^{19}F NMR δ ppm (CD_2Cl_2, 183.3 MHz): −66.1; MS (70 eV) m/z (^{74}Ge): 332 (M, 7), 303 (100), 275 (22), 245 (10), 181 (10), 151 (50), 133 (16), 115 (10). **2g**: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 6.82 (1H, d, $J=18$ Hz), 6.95 (1H, d, $J=18$ Hz), 7.15–7.7 (18Har, m); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 123.7, 125.2, 128.4, 128.6, 129.4, 129.8, 134.6, 135.4, 136.7, 141.0; MS (70 eV) m/z (^{74}Ge): 414 (M, 29), 303 (16), 257 (8), 226 (75), 186 (100), 151 (48). **2h**: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 0.8–1.2 (15H, m), 6.37 (1H, d, $J=19$ Hz), 6.88–7.18 (4H, m); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 4.7, 9.1, 124.6, 125.2, 127.7, 128.1, 136.3, 145.7; MS (70 eV) m/z (^{74}Ge): 270 (M, 4), 241 (100), 213 (49), 183 (16), 157 (26), 133 (8), 105 (18), 79 (32). **2i**: ^{1}H NMR δ ppm (CD_2Cl_2, 200 MHz): 7.05 (1H, d, $J=18.5$ Hz), 7.1–7.7 (19 H, m), 8.57 (1H, m); ^{13}C NMR δ (CD_2Cl_2, 50 MHz): 122.0, 123.1, 128.7, 129.5, 135.4, 136.4, 136.8, 146.9, 149.9, 155.5; MS (70 eV) m/z (^{74}Ge): 409 (M, 100), 330 (56), 305 (22), 254 (33), 227 (58), 180 (44), 151 (97), 104 (20), 74 (37), 59 (35), 45 (17).

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