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The preparation of pure allyl- and benzyl-type organoalkali intermediates via organotin compounds

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Abstract

Superbase metalation of alkenes or alkylbenzenes and subsequent condensation with trialkylstannyl chloride affords allyl- or benzyl-type organotin compounds that can be isolated in pure form. Treatment with soluble reagents such as methyllithium, trimethylsilylmethylpotassium and trimethylsilylmethylcaesium generates the corresponding organoalkali derivatives almost quantitatively and in high purity, suitable for kinetic or spectroscopic studies.

The preparation of organoalkali compounds free from by-products is by no means a trivial task. The standard procedures [1] such as the insertion of elementary metal into a carbon-halide or carbon–oxygen bond give rise to a salt-like "waste" product which is at least partially soluble in ethereal solvents and thus may affect the reactivity of the organometallic species [2]. The halogen/metal permutational exchange between organic bromides or iodides and alkyllithium reagents leads not only to a new organometallic compound but also to a new alkyl halide which only in favourable cases can be removed from the mixture by extraction [3]. Allyl- and benzyl-type organometallics are particularly troublesome to obtain since their precursors tend to undergo coupling reactions.

In the course of our continuing studies on the structure [4] and reactivity [5] of 2-alkenylpotassium species, we found it necessary to obtain such reagents with unprecedented purity. Previous reports on the successful generation of allyl- [6], 2-methylallyl- [6], crotyl- [6], benzyl- [7] and cyclohexyllithium [8] from organotin compounds and phenyllithium led us to investigate the use of a similar approach for our purpose. 2-Alkenyl-trimethylstannanes, 2-alkenyltributylstannanes, and benzyltributylstannane were found to undergo a rapid metal/metal permutation when treated with amalgam-free trimethylsilylmethylpotassium [9] in tetrahydrofuran. Similarly, allyl or benzyl type organolithium and organocaesium species can be generated by treatment of the organotin compound with methyllithium or trimethylsilylmethylcaesium [9], respectively (see Table 1).

The by-product, a (trialkylstannylmethyl)trimethylsilane or tetraalkylstannane, can be removed by evaporation under high vacuum and repeated washing with

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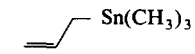
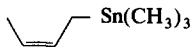
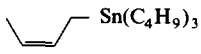
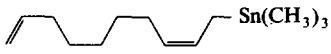
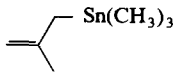
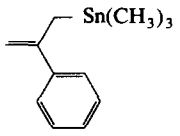
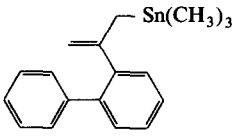
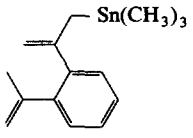
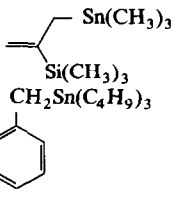
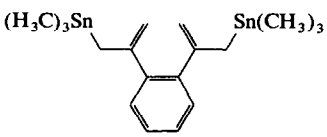
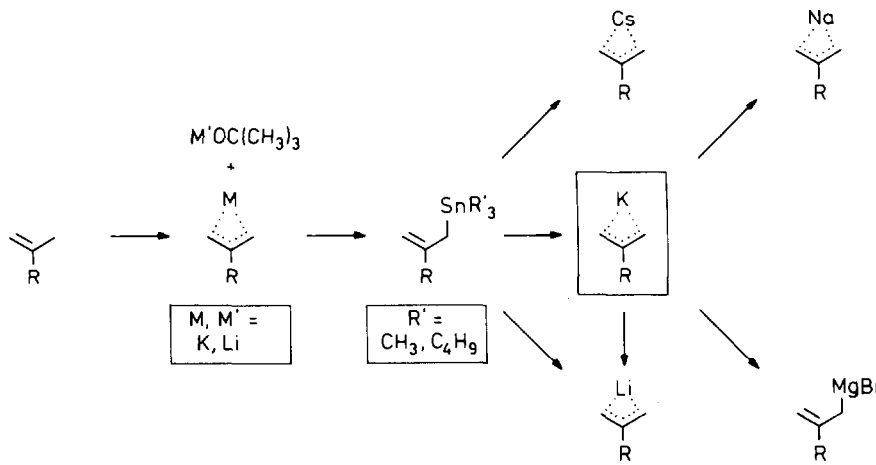
Table 1

Allyl- and benzyl-type organolithium, -potassium and -ceasium compounds prepared from the corresponding organotin derivatives by metalloid/metal permutation

Organotin compounds	Lithium deriv. (%)	Potassium deriv. (%)
	95 [a]	–
	–	97 [b]
	–	86 [b]
	90 [c,d]	93 [c,d]
	–	99 [e]
	64 [b]	94 [b]
	74 [b]	63 [b]
	85 [f]	95 [d]
	–	95 [a,g]
	93 [d]	97 [a,g]
	–	69 [c,d]
	77 [f]	82 [f]

[a] From the NMR spectrum (signal integration relative to tetramethylstannane). [b] Trapped with chlorotrimethylsilane. [c] Starting from 1,8-nonadiene, the analogous C_9 mono- and distannanes were prepared (see Experimental). [d] Trapped with methyl iodide. [e] Trapped with oxirane. [f] Trapped with dimethyl sulfate. [g] The caesium rather than the potassium derivative.

hexane. The resulting powder may then be dissolved in tetrahydrofuran. Such solutions should be stored at low temperatures (0 to $-50\,^{\circ}C$), especially in the case of organopotassium compounds. It is noteworthy that the latter can be readily converted into the magnesium, lithium or sodium analogs by simply adding a solution of magnesium dibromide, lithium bromide or sodium tetraphenylborate in tetrahydrofuran. The completely insoluble potassium salt precipitates out instantaneously [10].



Allyl- and benzyl-type organotin compounds can be readily generated by simple metalation of the corresponding alkene or alkylbenzene hydrocarbon with the superbasic mixture of butyllithium and potassium tert-butoxide [5,10] and by subsequent condensation of the mixed metal intermediate with trimethyl- or tributyl-stannyl chloride. If the substrate is prone to polymerization the yields are only moderate to good, but otherwise they are good to excellent (see Experimental).

Asymmetrically substituted organometallic intermediates react with chlorotrialkylstannanes to form preferentially, if not exclusively the regioisomer having the metalloid group at the free terminus of the allyl moiety. 2-Butenylpotassium or other 2-alkenylpotassium compounds [5,11] having the *endo* configuration are thus converted into *cis*-2-alkenylstannanes, which lose their stereochemical homogeneity only slowly at temperatures above $150\,^{\circ}C$. On the other hand, *exo*-2-alkenylpotassium intermediates invariably produce *cis/trans* mixtures of allyl-type stannanes. The mechanistic implications of this stereomutation will be discussed elsewhere.

Allyl-type stannanes are versatile carbonucleophiles, which may be employed in radical chain type, inter- or intramolecular (cyclizing) carbon–carbon linking reactions with alkyl halides [12,13], in stereocontrolled inter- or intra-molecular addition reactions with aldehydes [14,15] or aldimines [16], and a variety of other reactions [17]. Regio- and stereo-selective methods for their preparation are thus very welcome, especially if they are as simple as that described here.

Experimental

General

Starting materials were purchased from Fluka AG (Buchs), Aldrich-Chemie (Steinheim), or Merck-Schuchardt (Darmstadt), unless otherwise indicated below. Butyllithium was supplied by CheMetall, Frankfurt and potassium tert-butoxide by Hüls, Troisdorf. All commercial reagents were used without further purification. Air- and moisture-sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were stored and handled under 99.995% pure nitrogen. Tetrahydrofuran was obtained anhydrous by distillation after the characteristic blue color of *in situ* generated sodium diphenylketyl [18] was observed to persist. When it was of poor quality it was pretreated with cuprous chloride [19] and potassium hydroxide pellets. Hexane was dried by careful azeotropic distillation. Ethereal extracts were dried with sodium sulfate. Before distillation of compounds prone to radical polymerization or sensitive to acids a spatula tip of hydroquinone or potassium carbonate, respectively, was added.

The temperature of dry ice methanol baths is shown generally as $-75\,^{\circ}C$, and "room temperature" (22–26 °C) as 25 °C. If no reduced pressure is specified, boiling ranges were those at atmospheric pressure (720 ± 25 mmHg).

When products were not isolated, their yields were determined by gas chromatography comparing their peak areas with that of an internal standard after appropriate calibration. Chromosorb G-AW of 80–100 mesh was used as the support in packed analytical columns (2 or 3 m long, 2 mm inner diameter) and Chromosorb G-AW of 60–80 mesh in preparative columns (3 or 6 m long, 1 cm inner diameter). Packed columns were made of glass but capillary columns ($\geqslant$ 10 m long) of quartz ("fused silica").

Infrared spectra were recorded with films if the sample was liquid at room temperature, but with potassium bromide pellets in the case of solids. The intensities of absorption bands are abbreviated as s (strong), m (moderate), and w (weak).

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded at 250 MHz or, where indicated by an asterisk, at 360 MHz, and those of carbon nuclei at 90.6 MHz (with gated decoupling and external locking). Deuterochloroform was used as the solvent unless otherwise specified. The chemical shifts are relative to the signal from tetramethylsilane ($\delta = 0$ ppm). In the case of metal and metalloid compounds no internal standard was added, the chemical shifts being determined relative to the residual solvent peak (chloroform: $\delta(^1H)$ 7.27, tetrahydrofuran: $\delta(^1H)$ 3.58 and $\delta(^{13}C)$ 67.4 ppm). Coupling constants are given in Hz. The coupling patterns are characterized by abbreviations: s (singulet), d (doublet), t (triplet), q (quadruplet), pent (pentuplet), hex (hexuplet), dt (doublet of triplets) and m (multiplet).

The mass spectrum of the stannylated compounds showed no molecular peak under electron impact conditions, and so chemical ionization (c.i.) in an ammonia atmosphere at 95.3 eV was used. The molecular peak (M^+) listed refers to the most abundant isotope (^{120}Sn).

Elementary analyses were performed by the laboratory of I. Beetz, W-8640 Kronach.

Allyl and benzyl type organotin compounds

(a) Preparation and isolation. Butyllithium (40 mmol) in tetrahydrofuran (20 mL) was added dropwise to a cold (−75 °C) solution of the olefin (40 mmol) and potassium tert-butoxide (4.5 g, 40 mmol) in tetrahydrofuran (120 mL). After 5 h at −50 °C, the homogeneous mixture was added during 5 min to a solution of trimethylstannyl chloride (8.0 g, 40 mmol) in tetrahydrofuran (30 mL) kept at −75 °C. The mixture was subsequently allowed to warm to 25 °C then poured into water (0.5 L). The product was extracted with hexane (2 × 50 mL) and the organic layer washed with water (2 × 50 mL) and brine (100 mL). The solvent was evaporated and, if appropriate, the residue distilled under reduced pressure. Since the products were insufficiently stable for gas chromatographic analysis, their purities were checked by ^{1}H-NMR spectroscopy.

(b) Products. Allyltrimethylstannane [20]: 66%; b.p. 127–129 °C; n_D^{20} 1.4783; n_D^{25} 1.4750. IR: 3080 (m, ν(=C–H)), 2980 + 2910 + 2830 (s, ν(–C–H)), 1620 (s, ν(C=C)), 1190 (m, δ((Sn)CH_3), 880 (s, δ(C=CH_2)). ^{1}H-NMR*: 5.94 (1H, symm. m); 4.81 (1H, dm, *J* 16.9); 4.69 (1H, ddd, *J* 10.0, 2.0, 0.8); 1.80 (2H, dd, *J* 8.6, 1.2); 0.12 (9H, s).

cis-2-Butenyltrimethylstannane [21]: 59%; b.p. 72–73 °C/46 mmHg; n_D^{20} 1.4853; n_D^{25} 1.4827. IR: 3010 (s, ν(=C–H)), 2970 + 2910 + 2860 (s, ν(–C–H)), 1640 (m, ν(C=C)), 1450 (m, δ(CH_3)), 1420 (m, δ(CH=CH)), 1190 (m, δ((Sn)CH_3), 990 (m, δ(=C–H)). ^{1}H-NMR: 5.58 (1H, dtq, *J* 10.7, 9.4, 1.7); 5.20 (1H, dqm, *J* 10.6, 6.7); 1.74 (2H, dm, *J* 9.0); 1.57 (3 H, dm, *J* 6.8); 0.10 (9H, s). Analysis. Found C, 38.48; H, 7.33. $C_7H_{16}Sn$ (218.92) calc.: C, 38.41; H, 7.37%.

Trimethyl(1-methyl-2-propenyl)stannane [21]: 10% (together with 20% of both *cis*- and *trans*-2-butenyltrimethylstannane after treatment of crotylmagnesium bromide in tetrahydrofuran with chlorotrimethylstannane); b.p. (mixture) 68.0–72.5 °C/47 mmHg. ^{1}H-NMR: 6.06 (1H, symm. m); 4.71 (1H, dt, *J* 17.5, 1.5); 4.70 (1H, dt, *J* 11.7, 1.5); 2.11 (1H, pentt, *J* 7.0, 1.4); 1.28 (3H, d, *J* 7.1); 0.05 (9H, s).

cis-2-Butenyltributylstannane [22]: 63%; b.p. 112–13 °C/0.5 mmHg. ^{1}H-NMR: 5.58 (1H, dtq, *J* 10.5, 9.1, 1.7); 5.15 (1H, dqm, *J* 10.6, 6.7); 1.7 (2H, m); 1.6 (3H, m); 1.5 (6H, m); 1.3 (6H, hex-like m); 0.9 (15H, m).

Tributyl(1-methyl-2-propenyl)stannane (as a 1 : 4 mixture with *cis*-2-butenyltributylstannane resulting from the treatment of the organometallic intermediate with tributylstannyl chloride in a 1 : 1 mixture of tetrahydrofuran and hexane). ^{1}H-NMR: 6.11 (1H, ddd, *J* 17.7, 10.5, 7.2); 4.71 (1H, dt, *J* 17.3, 1.5); 4.68 (1H, dt, *J* 10.5, 1.5); 2.18 (1H, pentt, *J* 7.2, 1.4); 1.5 (6H, m); 1.32 (6H, hex, *J* 7.2); 1.3 (?, 3H, d, *J* ~ 7); 0.9 (15H, m). Analysis. Found: C, 55.59; H, 9.91. $C_{16}H_{34}Sn$ (345.16) calc.: C, 55.68; H, 9.93%.

Trimethyl(2-methyl-2-propenyl)stannane [23]: 39%; b.p. 142–143 °C; n_D^{20} 1.4795. IR: 3070 (m, ν(=C–H)), 2910 + 2850 (m, ν(–C–H)), 1630 (m, ν(C=C)), 1440 + 1380 (m, δ(CH_3)), 1190 (m, δ((Sn)CH_3)), 860 (m, δ(C=CH_2)). ^{1}H-NMR: 4.5 (2H, m); 1.80 (2H, d-like m); 1.70 (3H, dd, *J* 1.4, 0.7); 0.12 (9H, s). Analysis. Found: C, 38.61; H, 7.41. $C_7H_{16}Sn$ (218.92) calc.: C, 38.41, H, 7.37%.

Trimethyl(2,8-nonadienyl)stannane: 42%; b.p. 61–62 °C/0.1 mmHg; n_D^{20} 1.4895. MS (c.i.): 328 (0.3%, $M^+ + 2\ NH_4 + 4$), 304 (0.4%, $M^+ + NH_4 - 2$), 288 (0.7%, M^+), 273 (12%), 182 (100%). Analysis. Found: C, 50.95; H, 8.61. $C_{12}H_{24}Sn$ (287.03) calc.: C, 50.21; H, 8.43%.

(2,9-Decadienyl)trimethylstannane: 46%; b.p. 82–83°C/0.3 mmHg; n_D^{20} 1.4885. MS (c.i.): 302 (0.2%, M^+), 287 (0.9%), 257 (0.4%), 182 (100%). Analysis: Found: C, 52.62; H, 8.80. $C_{13}H_{26}Sn$ (301.06) calc.: C, 51.86; H, 8.71%.

Trimethyl(2-phenyl-2-propenyl)stannane: 31%; b.p. 68–69°C/0.1 mmHg: n_D^{20} 1.5542. ^{1}H-NMR: 7.4 (5H, m); 5.06 (1H, d, *J* 1.3), 4.88 (1H, dt, *J* 1.3, 1.1), 2.27 (2H, d, *J* 1.0); 0.00 (9H, s). MS (c.i.): 282 (3%, M^+), 267 (5%), 182 (100%). Analysis. Found: C, 51.48; H, 6.49. $C_{12}H_{18}Sn$ (280.99) calc.: C, 51.30; H, 6.46%.

2-(2-Biphenylyl-2-propenyl)trimethylstannane: 30%; b.p. 118–120°C/0.2 mmHg; n_D^{20} 1.5868. ^{1}H-NMR: 7.55 (2H, dm, *J* 7.5); 7.4 (7H, m); 4.96 (2H, symm. m); 1.63 (2H, s-like m); −0.16 (9H, s). MS (c.i.): 358 (0.4%, M^+), 343 (4%), 192 (100%), 179 (37%), 165 (24%). Analysis. Found: C, 62.99; H, 6.31. $C_{18}H_{22}Sn$ (357.08) calc.: C, 60.55; H, 6.21%.

Trimethyl-2-[2-(1-methylethenyl)phenyl]-2-propenylstannane: 50%; b.p. 83–85°C/0.1 mmHg; n_D^{20} 1.5524. IR: 3080 + 3060 (m, ν(=C–H)), 2920 (m, ν(–C–H)), 1630 + 1610 (m, ν(C=C)), 1450 (m, $\delta(CH_3)$), 1430 (m, $\delta(C{=}CH_2)$), 1190 (m, $\delta((Sn)CH_3)$), 890 + 870 (m, $\delta(C{=}CH_2)$), 760 (s, δ(=C–H)). ^{1}H-NMR*: 7.2 (4H, m); 5.15 (1H, dq, *J* 2.0, 1.3); 5.09 (1H, dd, *J* 2.0, 1.0); 4.92 (1H, dt, *J* 2.2, 1.0); 4.83 (1H, d, *J* 2.2); 2.23 (2H, d, *J* 1.0); 2.2 (3H, m); −0.07 (9H, s). MS: 322 (4%, M^+), 182 (100%), 165 (23%), 157 (45%). Analysis. Found: C, 56.34; H, 6.99. $C_{15}H_{22}Sn$ (321.05) calc.: C, 56.12; H, 6.91%.

Trimethyl(2-trimethylsilyl-2-propenyl)stannane: 45%; b.p. 33–34°C/1 mmHg; n_D^{20} 1.4816. IR: 3050 + 2980 (m, ν(=C–H), 2960 + 2900 (s + m, ν(–C–H)), 1580 (w, ν(C=C), 1420 (w, $\delta(C{=}CH_2)$), 1245 (m, $\delta((Si)CH_3)$), 1190 (w, $\delta((Sn)CH_3)$), 890 (m, δ $(C{=}CH_2)$). ^{1}H-NMR*: 5.35 (1H, dt, *J* 2.7, 1.2); 5.10 (1H, d, *J* 2.7); 1.95 (2H, d, *J* 1.3); 0.1 (9H, s); 0.09 (9H, s). Analysis. Found: C, 39.39; H, 8.20. $C_9H_{22}SiSn$ (277.07) calc.: C, 39.02; H, 8.00%.

Benzyltributylstannane [24]: 45%; b.p. 148–150°C/0.2 mmHg; n_D^{20} 1.5203. IR; 3070 + 3020 (w, ν(C=C–H)), 2920 + 2870 + 2850 (s + m + m, ν(–C–H)), 1600 (m, ν(C=C)), 1460 (m, (CH_2)), 1210 (m, $\delta((Sn)CH_2)$?), 750 + 690 (m, δ(=C–H)). ^{1}H-NMR: 7.16 (2H, t, *J* 7.7); 7.0 (3H, m); 2.30 (2H, s); 1.5 (6H, m); 1.3 (6H, m, hex-like); 0.87 (9H, t, *J* 7.1); 0.80 (6H, t, *J* 7.9). Analysis. Found: C, 59.90; H, 9.08. $C_{19}H_{34}Sn$ (381.19) calc.: C, 59.87; H, 8.99%.

2,7-Nonadienylenebis(trimethylstannane): 27% (metalation of 1,8-nonadiene performed in hexane at +25°C; details to be published elsewhere); b.p. 110–114°C/0.1 mmHg. MS (c.i.): 485 (0.2%, $M^+ + 2\ NH_4 - 3$), 467 (0.2%, $M^+ + NH_4 - 3$), 447 (0.5%, $M^+ - 3$), 287 (4%), 273 (94%), 182 (100%). Analysis. Found: C, 40.29, H, 7.22. $C_{15}H_{32}Sn_2$ (449.84) calc.: C, 40.05; H, 7.17%.

2,8-Decadienylenebis(trimethylstannane): 32% (metalation of 1,9-decadiene performed in hexane at +25°C; details to be published elsewhere); b.p. 118–120°C/0.1 mmHg. MS (c.i.): 504 (0.4%, $M^+ + 2\ NH_4 + 2$), 485 (0.4%, $M^+ + NH_4 + 1$), 466 (0.2%, M^+), 287 (34%), 182% (100%). Analysis. Found: 41.64; H, 7.36. $C_{16}H_{34}Sn_2$ (463.87) calc.: C, 41.43; H, 7.39%.

2,2′-*o*-Phenylenebis[trimethyl(2-propenyl)stannane]: 40% (metalation of 1,2-bis-(1-methylethenyl)benzene performed in diethyl ether at −75°C; details to be published elsewhere); b.p. 119–120°C/0.3 mmHg; n_D^{20} 1.5528. IR: 3090 + 3080 (m, ν(=C–H)), 2930 (m, ν(–C–H)), 1610 (m, ν(C=C)), 1430 (w, $\delta(C{=}CH_2)$), 1190 (m, $\delta((Sn)CH_3)$), 870 (m, $\delta(C{=}CH_2)$), 760 (m, δ(=C–H)). ^{1}H-NMR*: 7.5 (4H, symm. m); 4.90 (2H, dt, *J* 2.0, 1.0); 4.79 (2H, d, *J* 2.0); 2.35 (4H, d, *J* 1.0); −0.11 (18 H,

s). MS (c.i.): 504 (0.1%, $M^+ + NH_4$), 486 (1%), 321 (2%), 306 (31%), 182 (100%). Analysis. Found: C, 44.77; H, 6.06. $C_{18}H_{30}Sn_2$ (483.86) calc.: C, 44.68; H, 6.25%.

Conversion of organotin into organoalkali compounds

(a) Metaloïd / metal exchange followed by an NMR investigation. The precooled solution of the organoalkali reagent (methyllithium, trimethylsilylmethylpotassium or trimethylsilylmethylcaesium, 0.5 mmol in each case), in tetrahydrofuran-d_8 (5 mL) was added to a solution of the organotin compound (0.5 mmol) in tetrahydrofuran-d_8 (C_4D_8O, 2.5 mL) kept at $-100\,^\circ C$. After 3 h at $-100\,^\circ C$ and 1 h at $-75\,^\circ C$, (3 H at $-75\,^\circ C$ when methyllithium was used), the mixture was centrifuged under dry-ice cooling and an aliquot (approx. 1 mL) was transferred by means of a pipette to an NMR tube. The latter was placed in liquid nitrogen ($-200\,^\circ C$), evacuated (10^{-1} mmHg) and flame sealed. A ^{1}H-NMR spectrum was recorded at $-100\,^\circ C$. Samples for ^{13}C-NMR spectroscopy were prepared similarly except that ordinary tetrahydrofuran (C_4H_8O) was used as the solvent.

2-Phenylallyllithium: ^{1}H-NMR* (C_4D_8O): 7.61 (2H, dm, *J* 7.7); 7.09 (2H, tm, *J* 7.2); 7.01 (1H, tm, *J* 7.2); 2.53 (2H, s); 2.16 (2H, s). ^{13}C-NMR (C_4H_8O): 158.9 (1C, s); 149.5 (1C, s); 126.4 (2C, d, *J* 156); 126.1 (2C, d, *J* 157); 124.4 (1C, d, *J* 158); 52.6 (2C, t, *J* 143).

2-Phenylallylpotassium: ^{1}H-NMR* (C_4D_8O): 7.69 (2H, d, *J* 7.4); 7.1 (3H, m); 2.56 (2H, s); 2.23 (2H, s). ^{13}C-NMR (C_4H_8O): 154.3 (1C, s); 149.9 (1C, s); 126.5 (4C, d, *J* 156); 124.9 (1C, d, *J* 157); 52.6 (2C, t, *J* 147).

2-[2-(1-Methylethenyl)phenyl]allyllithium: ^{1}H-NMR* (C_4D_8O): 7.29 (1H, d, *J* 7.1); 7.0 (3H, m); 4.78 (2H, s); 2.52 (2H, s); 2.30 (3H, s); 1.92 (2H, s). ^{13}C-NMR (C_4H_8O): 162.4 (1C, s); 151.5 (1C, s); 150.0 (1C, s); 140.7 (1C, s); 128.5 (1C, d, *J* 159), 128.2 (1C, d, *J* 159); 125.8 (1C, d, *J* 156), 124.1 (1C, d, *J* 158); 110.3 (1C, t, *J* 153); 56.0 (2C, t, *J* 143); 22.3 (1C, q, *J* 127).

2-[2-(1-Methylethenyl)phenyl]allylpotassium: ^{1}H-NMR* (C_4D_8O): 7.4 (1H, m); 6.95 (3H, s); 4.83 (1H, s); 4.81 (1H, s); 2.56 (2H, s); 2.34 (3H, s); 1.86 (2H, s). ^{13}C-NMR (C_4H_8O): 157.0 (1C, s); 150.7 (1C, s); 150.5 (1C, s); 141.5 (1C, s); 128.7 (1C, d, *J* 156); 127.5 (1C, d, *J* 154); 125.0 (1C, d, *J* 153); 123.7 (1C, d, *J* 156); 109.8 (1C, t, *J* 156); 57.2 (2C, t, *J* 154); 25 (?, 1C, q, $J \sim 125$).

2-(Trimethylsilyl)allylcaesium: ^{1}H-NMR* (C_4D_8O): 2.52 (2H, s-like m); 2.48 (2H, s-like m); -0.02 (9H, s).

Benzylcaesium: ^{1}H-NMR* (C_4D_8O): 6.01 (2H, t, *J* 7.2); 5.36 (2H, d, *J* 8.0); 4.73 (1H, t, *J* 6.5); 2.31 (2H, s).

(b) Metaloïd / metal exchange followed by electrophilic trapping. The precooled solution of the organometallic reagent (methyllithium or trimethylsilylmethylpotassium, 10 mmol) in tetrahydrofuran (100 mL) was added slowly to a solution of the organotin compound (10 mmol) in tetrahydrofuran (50 mL) kept at $-100\,^\circ C$. After 3 h at $-75\,^\circ C$ (in case of lithium reagents) or 3 h at $-100\,^\circ C$ and 1 h at $-75\,^\circ C$ (in case of potassium reagents), the electrophile (20 mmol) was added. A sample (approx. 5 mL) with withdrawn and an inert reference substance ("internal standard") such as cyclododecane was added. The product composition and yields were determined by gas chromatographic comparison of their retention times with those of authentic samples and yields were determined by the integration of peak areas relative to that of the standard. The bulk solution was concentrated and partitioned

between hexane (100 mL) and brine (100 mL). The produce was isolated by distillation of the organic layer.

The metaloïd/metal exchange produces tetramethylstannane or trimethyl(trimethylstannylmethyl)silane as a by-product. In general, these stannanes do not interfere with the subsequent reaction and so may be left in the mixture. If desired, however, they can be removed before the electrophile is added. To this end, the allyl type organoalkali reagent has to be generated in dimethyl or diethyl ether rather than in tetrahydrofuran, but otherwise the procedure as described in the preceding paragraph is used. The ether is then evaporated at $-50\,^{\circ}C$ under high vacuum. The residue is extracted several times with hexane and the residual organometallic material is rigorously dried and finally dissolved in the chosen solvent, for example tetrahydrofuran.

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