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General access to *para*-substituted styrenes

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Abstract

A simple and efficient procedure has been developed for the synthesis of organogermanium compounds and styrenes *para*-substituted with groups containing an atom of the 14th group by one-pot reaction of halogenosilanes, germanes or stannanes, organic halides and magnesium using ultrasound methods.

Keywords: Organogermanium compounds; Styrene; Sonication

Inertial confinement fusion (ICF) experiments involve polymer capsules in which nuclear products are located [1]. The polymer capsule is composed of organic material which is a copolymer polystyrene-modified polystyrene. The capsule characteristics mainly depend on the average molecular weight, the molecular dispersity and finally the atomic composition. The modifications needed for the modified polystyrene are, e.g. the introduction of organometallic species (from Group 14) on the aromatic ring and also the presence of a spacer between the aromatic ring and the metal (Scheme 1).

For this purpose, we developed simple procedures for the synthesis of various modified styrene monomers doped with elements of Group 14 (silicon, tin and particularly with germanium atoms). Large-scale (5–7 g) synthesis of monomers was required for the polymerisation in order to obtain corresponding polymers or copolymers and to test their physical properties.

The chemistry of the carbon–germanium bond has previously been studied in detail and this bond is normally obtained by the reaction of germanium halides with organomagnesium (or organolithium) compounds [2,3]. The yield of the desired product is highly dependent on the accessibility of the organomagnesium reactant [4]. As shown by the numerous specific reports on the study of sonochemical reactions, the interest of synthetic chemists is becoming increasingly focused on the use of sonochemical methods in organic synthesis [5–10].

We first tested a simplified and improved one-step synthesis of organogermane compounds by Barbier reaction between germanium halides, magnesium turnings and organic halides using ultrasound without the presence of dibromoethane, as previously recommended for organotin synthesis [11] (Scheme 2).

A wide range of germanes **1a**–**1m** were subjected to this procedure to produce quite high yields of the corresponding products. A clean double-substitution reaction was also possible with dihalogenogermanium compounds and yielded difunctional germanium products **1n**–**1p**. The results are presented in Table 1.

As can be seen, this methodology can accommodate a variety of organic functional halides. The yields are nearly quantitative but need certain optimisation conditions for substituted allylic halides (e.g. entry 4) [12]. It should be noted that the quality of the reactants is not critical (solvent or halides), they do not need careful purification before use and dibromoethane is not necessary to start the reaction.

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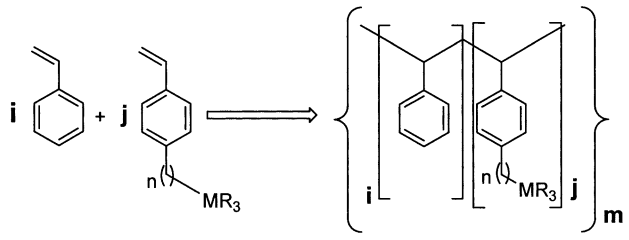
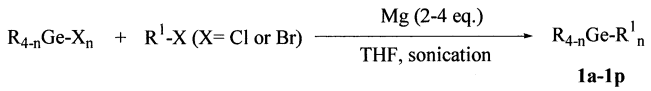


Scheme 1.

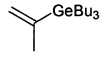
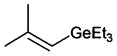
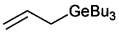
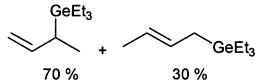
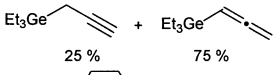
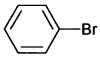
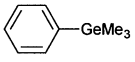
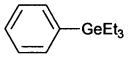
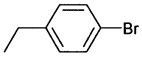
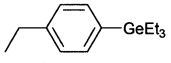
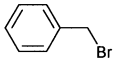
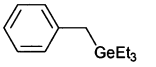
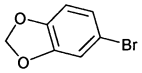
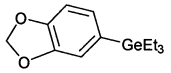
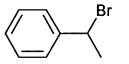
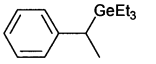
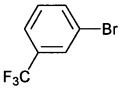
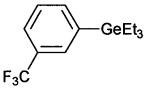
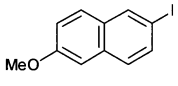
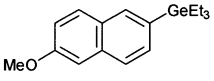
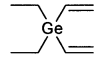
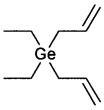
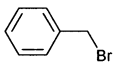
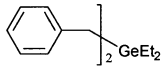


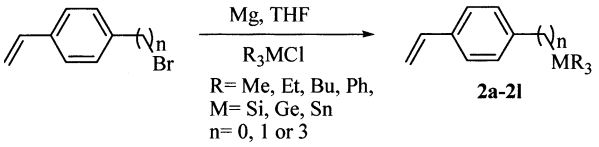
Scheme 2.

As we obtained various compounds, we decided to extend this methodology to the synthesis of styrene *para*-substituted with groups containing a Group 14 element (Scheme 3).

Some styrenes with an $n = 0$ spacer have previously been reported and are based on the addition of silicon, germanium or tin halides to *p*-vinylphenylmagnesium with acceptable yields (55–70%) [13] and with an $n = 1$ spacer from 4-vinylbenzyllithium [14] or 4-vinylbenzylmagnesium [15]. For the last two, yields were moderate to low and the desired products were always polluted with various by-products and needed careful purification [16]. In our case, where large quantities are required, this is a major drawback.

Table 1
Synthesis of various organogermanium compounds

$R_nGe\text{-}X_{4-n}$	R'-X	$R_nGe\text{-}R'_{4-n}$	Yield %	N°
Bu_3GeCl			83	**1a**
Et_3GeBr			82	**1b**
Bu_3GeCl			95	**1c**
Et_3GeBr		 70 % 30 %	74	**1d + 1d'**[12]
"		 25 % 75 %	90	**1e + 1e'**
Me_3GeBr			85	**1f**
Et_3GeBr	"		78	**1g**
Et_3GeBr			79	**1h**
"			80	**1i**
"			76	**1j**
"			81	**1k**
"			56	**1l**
"			68	**1m**
Et_2GeCl_2	$CH_2{=}CH_2MgBr$		80	**1n**
"			85	**1o**
"			82	**1p**



Scheme 3.

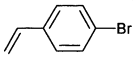
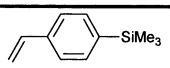
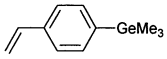
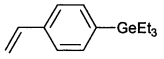
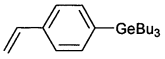
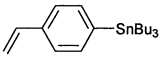
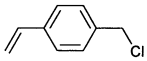
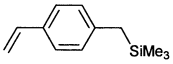
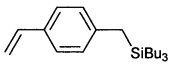
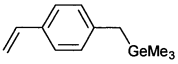
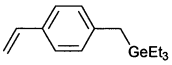
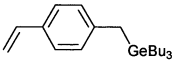
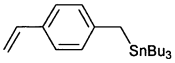
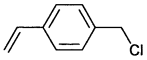
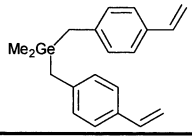
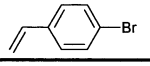
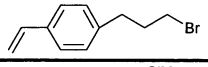
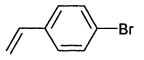
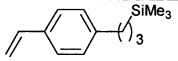
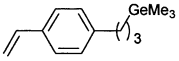
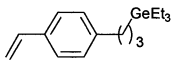
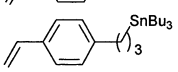
The present procedure provides an efficient one-pot synthesis of *para*-substituted styrene monomers **2a**–**2l** with $n = 0$ or 1 spacer. The results are shown in Table 2.

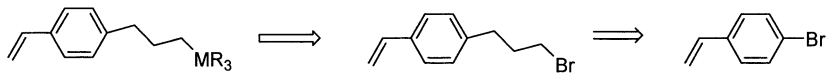
The notable advantages of this procedure are operational simplicity, fast reaction, and in comparison with the typical (and older) reaction of germanium halides with organomagnesium (or organolithium) compounds for the creation of the carbon–germanium bond, high yields are obtained. For example, for entries 8 and 9 in Table 2, we can compare the 74 and 72% yields under ultrasound conditions, and 11% yield under classical conditions [14c,14d]. No product resulting from polymerisation of the styrene monomers was detected and very small amounts of duplicated bibenzyl products were found ($< 5\%$).

To introduce a three-carbon spacer between the phenyl group and the trialkyl (or triphenyl) metal group, the case under consideration is shown in the retrosynthetic scheme (Scheme 4).

With a double-ultrasound reaction starting from *p*-bromostyrene and 1,3-dibromopropane, we synthesised

Table 2
Synthesis of *para*-substituted trialkyl (or triphenyl)silyl, germyl or stannyl styrenes

Entry	$R_nM\text{-}X_{4-n}$	R'-X	$R_n\text{-}M\text{-}R'_{4-n}$	Yield %	N°
1	Me_3SiCl			82	**2a**
2	Me_3GeBr			89	**2b**
3	Et_3GeBr	"		78	**2c**
4	Bu_3GeCl	"		91	**2d**
5	Bu_3SnCl	"		64	**2e**
6	Me_3SiCl			86	**2f**
7	Bu_3SiCl	"		76	**2g**
8	Me_3GeBr	"		74	**2h**
9	Et_3GeBr	"		72	**2i**
10	Bu_3GeCl	"		49	**2j**
11	Bu_3SnCl	"		71	**2k**
12	Me_2GeCl_2				**2l**
13	none			72	**3**
14	Me_3SiCl			56	**4a**
15	Me_3GeCl	"		61	**4b**
16	Et_3GeCl	"		66	**4c**
17	Bu_3SnCl	"		63	**4d**



Scheme 4.

styrenes **4a**–**4d** (Table 2) with a three-carbon spacer. The overall yield from the *p*-bromostyrene was about 40% after purification and no by-products were detected (Scheme 5).

In conclusion, we describe new procedures allowing efficient one-pot synthesis of functional organogermanium compounds from expensive germanium halides. Large-scale synthesis of a wide range of *para*-substituted styrenes was also performed with acceptable overall yields (from 49 to 91%). The main advantages of these procedures are (a) operational simplicity, (b) fast reaction, and (c) high yield. We believe that this will provide a better and more practical alternative to the existing methods for the synthesis of germanium compounds. Some of these new styrene compounds are currently being tested for copolymerisation with styrene and are providing promising results in terms of molecular weight, low polydispersity and physical properties (mechanical, thermal and solubility). The polymerisation process and characterisation of these polymers are currently under way and will be reported in due course.

1. Experimental

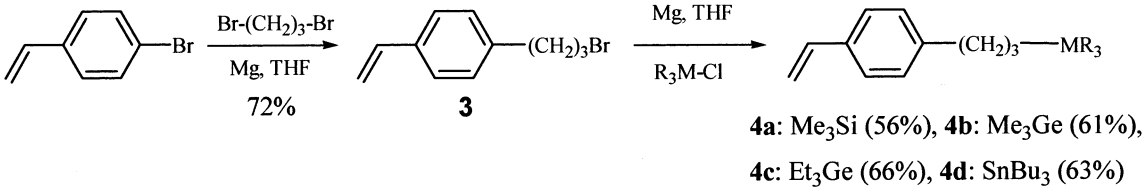
All reactions were carried out under an inert atmosphere (Ar or N_2). Flash chromatography was performed with Merck silica gel (silica gel, 230–400 meshes). ^{1}H-NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Bruker ARX 400 (400 MHz) nuclear magnetic resonance spectrometer using $CDCl_3$ as solvent. The findings reported using the residual solvent proton resonance of $CDCl_3$ ($\delta_H = 7.25$ ppm) were as follows (in order): chemical shift (δ in ppm relative to Me_4Si), multiplicity (s, d, t, q, m, b for singlet, doublet, triplet, quartet, multiplet, broad, respectively) and coupling constants (J in Hz). ^{13}C-NMR were recorded at 50.3 MHz on the same instruments using the $CDCl_3$ solvent peak at $\delta_C = 77.0$ ppm as reference. ^{19}F-NMR were recorded in $CDCl_3$ using C_6F_6 as external reference (^{19}F, −164.9 ppm). Analytical GC was carried out on a Chrompack CP 9002 gas chromatograph equipped with a flame ionisation detector. Mass spectra were obtained on a Hewlett Packard (engine 5989A) in the GC–MS (70 eV) mode. The isotopic patterns are given for ^{120}Sn (isotopic abundance: 33%) in organostannyl fragments and for ^{74}Ge (isotopic abundance: 36.6%) in organogermyl fragments. This means that the reported abundances (values in brackets) for organostannyl or organogermyl fragments are roughly only one-third of the correct value, taking into account the 10 isotopes of tin and the five isotopes of germanium compared with those of the organic fragment. IR spectra were recorded on a Perkin–Elmer 781 Infrared Spectrophotometer or on a Perkin–Elmer 1600 series FTIR spectrophotometer. Some compounds are commercially available **1f** or fully described such as **1g** [17], **1i** [18], **1p** [18], **2a** [19], **2b** [19], **2f** [19], **2h** [19].

1.1. General representative procedure under ultrasound conditions

A Schlenk tube containing 25 ml of THF, 0.60 g (25 mmol, two equivalent mole) of magnesium turnings, 2.5 mmol (one equivalent mole) of bromo- or chlorogermane and 2.28 g (12.5 mmol, one equivalent) of 4-bromostyrene is plunged into a commercial ultrasonic cleaning bath (Branson B1200 E1, working frequency: 47 kHz, 300 W) and sonicated for 2 h. The mixture is washed with a saturated solution of sodium chloride and extracted with diethylether. The organic layers are dried over magnesium sulphate, the solvents are removed under reduced pressure and the compound obtained is purified by column chromatography (petroleum ether/diethylether: 95/5).

1.1.1. 2-Tributylgermylpropene (**1a**) [20]

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.75–1.50 (27H, m), 1.82 (3H, s), 5.05 (1H, s), 5.52 (1H, s); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 14.2 (3C), 14.7, 18.2 (3C), 19.3 (3C), 26.8 (3C), 123.6, 148.4; MS (70 eV) *m/z*: 229 [M$^+$&z.rad;−57, 100], 173 (77), 131 (38), 117 (24), 89 (14).



Scheme 5.

*1.1.2. 1-Triethylgermyl-2-methylprop-1-ene (**1b**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.68–1.04 (15H, m), 1.69 (3H, s), 1.81 (3H, s), 5.18 (1H, s); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 6.1 (3C), 8.5 (3C), 24.3, 29.2, 121.9, 150.4; MS (70 eV) *m/z*: 216 [M$^+$&z.rad, 6], 187 (100), 159 (64), 131 (52), 101 (11), 89 (12).

*1.1.3. 3-Tributylgermylprop-1-ene (**1c**) [21]*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.67–1.46 (27H, m), 1.63 (2H, d, $J = 8.3$ Hz), 4.74 (2H, dd, $J = 16.8$ Hz, $J = 9.8$ Hz), 5.7 (1H, ddt, $J = 16.8$ Hz, $J = 9.8$ Hz, $J = 8.4$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 12.9 (3C), 14.2 (3C), 19.7 (3C), 26.3 (3C), 27.3, 112.2, 137.1; MS (70 eV) *m/z*: 286 [M$^+$&z.rad, 3], 245 (53), 223 (24), 189 (100), 167 (14), 131 (59), 103 (10), 89 (15).

*1.1.4. 3-Triethylgermylprop-1-yne (**1e**) [22]*

Obtained after column chromatography of the mixture. ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.74–1.11 (15H, m), 1.52 (2H, d, $J = 2.9$ Hz), 1.78 (1H, t, $J = 2.9$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 0.8, 4.9 (3C), 9.7 (3C), 67.0, 78.8; MS (70 eV) *m/z*: 200 [M$^+$&z.rad, 4], 171 (38), 161 (100), 143 (27), 133 (65), 113 (27), 103 (54), 75 (10).

*1.1.5. 1-Triethylgermyl-4-ethylbenzene (**1h**)*

IR: 3064, 3009, 2956, 2930, 2905, 2871, 1460, 1377, 1090, 1013, 817; ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.99–1.10 (15H, m), 1.25 (3H, t, $J = 7.6$ Hz), 2.65 (2H, q, $J = 7.6$ Hz), 7.20 (2H$_{ar}$, d, $J = 8.0$ Hz), 7.37 (2H$_{ar}$, d, $J = 8.0$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.4 (3C), 9.0 (3C), 15.8, 29.0, 127.9 (2C), 134 (2C), 137.0, 144.7; MS (70 eV) *m/z*: 266 [M$^+$&z.rad, 6], 237 (100), 209 (44), 179 (52), 105 (15).

*1.1.6. 1-Triethylgermyl-3,4-methylenedioxybenzene (**1j**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.93–1.09 (15H, m), 5.91 (2H, s), 6.82–6.92 (3H$_{ar}$, m); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.6 (3C), 9.0 (3C), 101.6, 108.8, 113.6, 127.6, 132.7, 147.8, 148.0; MS (70 eV) *m/z*: 282 [M$^+$&z.rad, 29], 253 (100), 225 (57), 195 (61), 182 (15).

*1.1.7. α-(Triethylgermyl)-ethylbenzene (**1k**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.73 (6H, q, $J = 8.1$ Hz), 0.98 (9H, t, $J = 8.1$ Hz), 1.45 (3H, d, $J = 8.1$ Hz), 2.55 (1H, q, $J = 7.6$ Hz), 7.01–7.27 (5H$_{ar}$, m); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 3.3 (3C), 9.2 (3C), 16.4, 28.3, 124.5, 127.1 (2C), 128.5 (2C), 147.8; MS (70 eV) *m/z*: 266 [M$^+$&z.rad, 54], 237 (20), 161 (97), 133 (100), 105 (51), 77 (12).

*1.1.8. 3-Triethylgermyl-1-trifluoromethylbenzene (**1l**) [23]*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 1.04–1.08 (15H, m), 7.43–7.70 (4H, m); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.6 (3C), 9.1 (3C), 125.0 (q, $J_{C-F} = 272$ Hz), 125.1, 130.5, 130.7 (q, $J_{C-F} = 31$ Hz), 130.7, 137.9, 141.9; ^{19}F-NMR δ ppm ($CDCl_3$, 188 MHz): −66.0.

*1.1.9. 2-Triethylgermyl-7-methoxynaphthalene (**1m**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.84–1.15 (15H, m), 3.92 (3H, s), 7.1–7.8 (6H$_{ar}$, m); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.5 (3C), 8.2 (3C), 55.6, 105.6, 106.0, 118.8, 119.0, 129.1, 129.6, 134.1, 134.1, 134.9, 158.0; MS (70 eV) *m/z*: 318 [M$^+$&z.rad, 18], 289 (100), 261 (40), 231 (49), 186 (10).

*1.1.10. Diethyldivinylgermane (**1n**) [24]*

Dichlorodiethylgermane was sonicated with a commercial 1 M solution of vinylmagnesium bromide in THF. ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.82–1.16 (10H, m), 5.66 (2H, dd, $J = 19.6$ Hz, $J = 3.8$ Hz), 6.04 (2H, dd, $J = 13.6$ Hz, $J = 3.8$ Hz), 6.27 (2H, dd, $J = 19.6$ Hz, $J = 13.6$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 5.3 (2C), 9.2 (2C), 131.8 (2C), 136.8 (2C); MS (70 eV) *m/z*: 157 [M−29, 100], 128 (27), 101 (81), 74 (28), 73 (23), 71 (11), 59 (26), 45 (23), 41 (11).

*1.1.11. Diallyldiethylgermane (**1o**) [25]*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.81 (6H, q, $J = 7.9$ Hz), 1.05 (4H, t, $J = 7.9$ Hz), 1.73 (4H, d, $J = 8.2$ Hz), 4.81 (2H, dd, $J = 9.8$ Hz, $J = 1.1$ Hz), 4.88 (2H, dd, $J = 16.7$ Hz, $J = 1.1$ Hz), 5.86 (2H, ddt, $J = 16.7$ Hz, $J = 9.8$ Hz, $J = 8.2$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.6 (2C), 9.6 (2C), 19.3 (2C), 112.6 (2C), 136.4 (2C); MS (70 eV) *m/z*: 173 (69), 145 (50), 115 (40), 103 (100), 74 (10), 41 (14), 39 (20).

1.2. Synthesis of para-substituted styrenes

They were obtained by the same methodology as described before.

*1.2.1. 4-Triethylgermylstyrene (**2c**) [26]*

IR: 2956, 2868, 1629, 1461, 1390, 825; ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.90–1.20 (15H, m), 5.24 (1H, d, $J = 10.9$ Hz), 5.79 (1H, d, $J = 17.6$ Hz), 6.73 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.39 (2H$_{ar}$, d, $J = 8.4$ Hz), 7.43 (2H$_{ar}$, d, $J = 8.4$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.4 (3C), 9.0 (3C), 113.8, 125.9 (2C), 134.6 (2C), 137.3, 137.7, 140.1; MS (70 eV) *m/z*: 264 [M$^+$&z.rad, 17], 235 (100), 207 (50), 177 (47), 151 (14).

*1.2.2. 4-Tributylgermylstyrene (**2d**) [27]*

IR: 3061, 3007, 2956, 2924, 2870, 2855, 1629, 1464, 1388, 905, 826; ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.86–1.03 (15H, m), 1.33–1.40 (12H, m), 5.23 (1H, d, $J = 10.9$ Hz), 5.77 (1H, d, $J = 17.6$ Hz), 6.72 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.38 (2H$_{ar}$, d, $J = 8.35$ Hz), 7.42 (2H$_{ar}$, d, $J = 8.35$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 12.9 (3C), 13.9 (3C), 26.9 (3C), 27.7 (3C), 113.7, 125.8 (2C), 134.5 (2C), 137.3, 137.5, 141.0; MS

(70 eV) *m/z*: 348 [M^+&z.rad, 2], 291 (100), 235 (87), 179 (62), 151 (12).

*1.2.3. 4-Tributylstannylstyrene (**2e**) [27]*

IR: 2958, 2926, 1629, 1461, 1386, 907, 821; ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.87–0.94 (9H, m), 1.04–1.12 (6H, m), 1.29–1.40 (6H, m), 1.52–1.61 (6H, m), 5.23 (1H, d, $J = 10.9$ Hz), 5.78 (1H, d, $J = 17.6$ Hz), 6.71 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.36 ($2H_{ar}$, d, $J = 8.1$ Hz), 7.45 ($2H_{ar}$, d, $J = 8.1$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 9.9 (3C, $J_{Sn-C} = 340–326$ Hz), 13.9 (3C), 27.8 (3C, $J_{Sn-C} = 57–55$ Hz), 29.5 (3C, $J_{Sn-C} = 20.2$ Hz), 113.7, 125.9 (2C, $J_{Sn-C} = 42–40$ Hz), 137.1 (2C, $J_{Sn-C} = 30$ Hz), 137.4, 137.6, 142.4 ($J_{Sn-C} = 38–368$ Hz); MS (70 eV) *m/z*: 394 [M^+&z.rad, 1], 337 (81), 281 (52), 223 (100), 197 (12), 121 (12).

*1.2.4. 4-Tributylsilylmethylstyrene (**2g**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.87–1.35 (27H, m), 2.13 (2H, s), 5.16 (1H, d, $J = 10.9$ Hz), 5.69 (1H, d, $J = 17.6$ Hz), 6.70 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.00 ($2H_{ar}$, d, $J = 8.2$ Hz), 7.29 ($2H_{ar}$, d, $J = 8.2$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 12.1 (3C), 14.0 (3C), 26.4 (3C), 27.2 (3C or 1C), 27.3 (3C or 1C), 112.0, 126.4 (2C), 128.7 (2C), 133.7, 137.3, 141.3; MS (70 eV) *m/z*: 316 [M^+&z.rad, 10], 199 (84), 143 (100), 101 (17), 87 (13), 59 (10). Anal. Calc. for $C_{21}H_{36}Si$: C, 79.67; H, 11.46. Found: C, 79.65; H, 11.41%.

*1.2.5. 4-Triethylgermylmethylstyrene (**2i**)*

IR: 3015, 2949, 2904, 2870, 1628, 1509, 840; ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.70–0.78 (6H, q, $J = 7.1$ Hz), 0.96–1.04 (9H, t, $J = 7.1$ Hz), 2.23 (2H, s), 5.13 (1H, d, $J = 10.9$ Hz), 5.66 (1H, d, $J = 17.6$ Hz), 6.67 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 6.98 ($2H_{ar}$, d, $J = 8.1$ Hz), 7.26 ($2H_{ar}$, d, $J = 8.1$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.1 (3C), 8.9 (3C), 21.1, 111.9, 126.4 (2C), 128.2 (2C), 133.4, 137.2, 141.9; MS (70 eV) *m/z*: 278 [M^+&z.rad, 90], 249 (18), 219 (11), 191 (14), 161 (100), 133 (68), 117 (38), 103 (18). Anal. Calc. for $C_{15}H_{24}Ge$: C, 65.05; H, 8.73. Found: C, 65.15; H, 8.67%.

*1.2.6. 4-Tributylgermylmethylstyrene (**2j**)*

IR: 2956, 2924, 2870, 2855, 1629, 1464, 1376, 899, 839; ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.70–1.36 (27H, m), 2.24 (2H, s), 5.14 (1H, d, $J = 10.9$ Hz), 5.68 (1H, d, $J = 17.6$ Hz), 6.69 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 6.99 ($2H_{ar}$, d, $J = 8.2$ Hz), 7.26 ($2H_{ar}$, d, $J = 8.2$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 12.8 (3C), 14.1 (3C), 22.5, 27.2 (3C), 27.9 (3C), 111.9, 126.6 (2C), 128.5 (2C), 133.7, 137.4, 145.0; MS (70 eV) *m/z*: 362 [M^+&z.rad, 30], 245 (82), 189 (100), 165 (13), 133 (25), 117 (22), 91 (6).

*1.2.7. 4-Tributylstannylmethylstyrene (**2k**) [24,28]*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.88–1.00 (15H, m), 1.31–1.58 (12H, m), 2.40 (2H, s, $J_{Sn-H} = 57$ Hz), 5.17 (1H, d, $J = 10.9$ Hz), 5.71 (1H, d, $J = 17.6$ Hz), 6.72 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.03 ($2H_{ar}$, d, $J = 8.2$ Hz), 7.30 ($2H_{ar}$, d, $J = 8.2$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 9.8 (3C, $J_{Sn-C} = 318–303$ Hz), 14.1 (3C), 22.5, 28.0 (3C, $J_{Sn-C} = 55–52$ Hz), 29.6 (3C, $J_{Sn-C} = 20$ Hz), 111.6, 126.7 (2C), 127.6 (2C), 133, 137.4, 145.0; MS (70 eV) *m/z*: 408 [M^+&z.rad, 6], 351 (5), 291 (76), 235 (100), 179 (85), 117 (84); ^{119}Sn-NMR ($CDCl_3$, 74.2 Hz) δ ppm: −3.4.

*1.2.8. 4-Di(dimethylgermylmethyl)styrene (**2l**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.05 (6H, s), 2.25 (4H, s), 5.16 (2H, d, $J = 10.9$ Hz), 5.68 (2H, d, $J = 17.6$ Hz), 6.69 (2H, dd, $J = 10.9$ Hz, $J = 17.6$ Hz), 6.96 (4H, d, $J = 8.17$ Hz), 7.28 (4H, d, $J = 8.17$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): −4.4 (2C), 24.8 (2C), 112.1 (2C), 126.4 (4C), 128.3 (4C), 133.8 (2C), 137.1 (2C), 141.2 (2C); MS (70 eV) *m/z*: 338 [M^+&z.rad, 55], 221 (100), 117 (88), 91 (15).

*1.2.9. 1-Bromo-3-p-styrylpropane (**3**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 2.15 (2H, m, $J = 6.8$ Hz), 2.76 (2H, t, $J = 6.8$ Hz), 3.41 (2H, t, $J = 6.8$ Hz), 5.21 (1H, d, $J = 10.9$ Hz), 5.73 (1H, d, $J = 17.6$ Hz), 6.71 (1H, dd, $J = 10.9$ Hz, $J = 17.6$ Hz), 7.17 ($2H_{ar}$, d, $J = 8.1$ Hz), 7.36 ($2H_{ar}$, d, $J = 8.1$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 33.6, 34.0, 34.5, 113.3, 126.5 (2C), 129.0 (2C), 140.2, 140.8, 144.8.

*1.2.10. 1-Trimethylsilyl-3-p-styrylpropane (**4a**)*

IR: 3100, 3015, 1640, 1520, 1420, 1260, 1000; ^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.09 (9H, s), 0.64 (2H, m), 1.71 (2H, m), 2.71 (2H, t, $J = 7.5$ Hz), 5.29 (1H, dd, $J = 10.9$ Hz, $J = 1$ Hz), 5.81 (1H, dd, $J = 17.6$ Hz, $J = 1$ Hz), 6.80 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.24 ($2H_{ar}$, d, $J = 8.1$ Hz), 7.44 ($2H_{ar}$, d, $J = 8.1$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): −1.7 (3C), 16.5 ($J_{Si-C} = 51$ Hz), 26.0, 39.6, 112.7, 126.1 (2C), 128.6 (2C), 135.0, 136.7, 142.4; MS (70 eV) *m/z*: 218 [M^+&z.rad, 6], 101 (10), 73 (100), 59 (13), 45 (12); ^{29}Si-NMR δ ppm: 1.42, $J_{Si-H} = 6.5$ Hz. Anal. Calc. for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 77.05; H, 9.89%.

*1.2.11. 1-Trimethylgermyl-3-p-styrylpropane (**4b**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.16 (9H, s), 0.78–1.00 (2H, m), 1.65–1.75 (2H, m), 2.64 (2H, t, *J*), 5.22 (1H, dd, $J = 10.9$ Hz, $J = 1$ Hz), 5.74 (1H, dd, $J = 17.6$ Hz, $J = 1$ Hz), 6.74 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.18 ($2H_{ar}$, d, $J = 8.2$ Hz), 7.37 ($2H_{ar}$, d, $J = 8.2$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): −2.3 (3C), 16.9, 27.6, 39.7, 112.9, 126.4 (2C), 129.0 (2C), 135.4, 137.1, 143.0; MS (70 eV) *m/z*: 264 [M^+&z.rad, 12], 249 (84), 236 (28), 119 (100), 105 (26), 91 (13).

*1.2.12. 1-Triethylgermyl-3-p-styrylpropane (**4c**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.72–1.07 (17H, m), 1.55–1.75 (2H, m), 2.63 (2H, t, $J = 6.9$ Hz), 5.20 (1H, dd, $J = 10.9$ Hz, $J = 1$ Hz), 5.72 (1H, dd, $J = 17.6$ Hz, $J = 1$ Hz), 6.72 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.16 ($2H_{ar}$, d, $J = 8.2$ Hz), 7.35 ($2H_{ar}$, d, $J = 8.2$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 4.4 (3C), 9.1 (3C), 13.9, 24.9, 38.0, 112.8, 126.4 (2C), 129.0 (2C), 135.4, 137.0, 143.0. Anal. Calc. for $C_{17}H_{28}Ge$: C, 66.94; H, 9.25. Found: C, 66.85; H, 9.19%.

*1.2.13. 1-Tributylstannyl-3-p-styrylpropane (**4d**)*

^{1}H-NMR δ ppm ($CDCl_3$, 200 MHz): 0.81–1.58 (29H, m), 1.82 (2H, m), 2.61 (2H, t, $J = 6.8$ Hz), 5.19 (1H, dd, $J = 10.9$ Hz, $J = 1$ Hz), 5.72 (1H, dd, $J = 17.6$ Hz, $J = 1$ Hz), 6.71 (1H, dd, $J = 17.6$ Hz, $J = 10.9$ Hz), 7.15 ($2H_{ar}$, d, $J = 8.1$ Hz), 7.34 ($2H_{ar}$, d, $J = 8.1$ Hz); ^{13}C-NMR δ ppm ($CDCl_3$, 50 MHz): 9.2 (3C, $J_{Sn-C} = 315–302$ Hz), 14.1 (3C), 28.0 (3C, $J_{Sn-C} = 51–53$ Hz), 29.8 (3C, $J_{Sn-C} = 20$ Hz), 29.7, 40.9 ($J_{Sn-C} = 54.2$ Hz), 113.0, 126.5 (2C), 129.2 (2C), 135.5, 137.1, 143.1; MS (70 eV) m/z: 436 [M^+&z.rad, 12], 380 (55), 291 (82), 117 (100), 104 (75).

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References

[1] F. David-Quillot, A. Duchêne, J.-M. Catala, A. Longeau, Fusion Sci. Technol. 41 (2002) 253.
[2] M. Lesbre, P. Mazerolles, J. Satgé, The Organic Compounds of Germanium, Wiley, New York, 1971.
[3] S. Patai, Z. Rappoport, The Chemistry of Organic Germanium, Tin and Lead Compounds, Wiley, Chichester, 1995.
[4] B.J. Wakefield, Organomagnesium Methods in Organic Synthesis, Academic Press, London, 1995.
[5] (a) C. Einhorn, J. Einhorn, J. Lurke, Sonochemistry—The Use of Ultrasonic Waves in Synthetic Organic Chemistry Synthesis, 1988, p. 787.;
(b) S.V. Ley, C.M.R. Low, Ultrasound in Synthesis, Springer, New York, 1989;
(c) T.J. Mason (Ed.), Sonochemistry: The Uses of Ultrasound in Chemistry, The Royal Society of Chemistry, Cambridge, 1990.
[6] (a) Y. Goldberg, R. Strukovich, E. Lukevics, Heterocycles 29 (1989) 597;
(b) Y. Goldberg, R. Strukovich, E. Lukevics, Synth. Commun. 23 (1993) 1235.
[7] T. Ando, T. Kimura, in: T.J. Mason (Ed.), Advances in Sonochemistry, vol. 2, JAI Press, London, 1991, pp. 211–251.
[8] (a) R. Davidson, in: T.J. Mason (Ed.), Sonochemistry: The Uses of Ultrasound in Chemistry, The Royal Society of Chemistry, Cambridge, UK, 1992, p. 50;
(b) J. Pestman, J. Engberts, F. Jong, Recl. Trav. Chim. Pays-Bas 113 (1994) 533.
[9] (a) R. Bowser, R. Davidson, in: G.J. Price (Ed.), Current Trends in Sonochemistry, The Royal Society of Chemistry, Cambridge, UK, 1992, pp. 50–58, 87–109;
(b) R.S. Varma, K.P. Naicker, Tetrahedron Lett. 40 (1999) 6177;
(c) J.-L. Luche, Synthetic Organic Sonochemistry, Plenum Press, New York, 1998.
[10] F. David-Quillot, S. Lunot, D. Marsacq, A. Duchêne, Tetrahedron Lett. 41 (2000) 4905.
[11] A. Lee, W. Dai, Tetrahedron 53 (1997) 859.
[12] (a) J. Yamaguchi, Y. Tamada, T. Takeda, Bull. Soc. Chim. Jpn. 66 (1993) 607;
(b) T. Nakano, K. Ono, T. Migita, Chem. Lett. (1996) 697;
(c) T. Nakano, S. Noda, N. A-Ihara, H. Yamashita, T. Miyamoto, T. Migita, T. Enokido, M. Kosugi, Main Group Met. Chem. 24 (2002) 67;
(d) T. Nakano, K. Ono, T. Migita, J. Organomet. Chem. 619 (2001) 313.
[13] (a) J. Leebrick, H. Ramsden, J. Org. Chem. 23 (1958) 935;
(b) J. Noltes, H. Budding, G. Van der Kerck, Recl. Trav. Chim. Pays-Bas 79 (1960) 408, 1076.
[14] (a) Y. Nagasaki, T. Tsuruta, Makromol. Chem. Rapid Commun. 7 (1986) 437;
(b) Y. Nagasaki, K. Kurosowa, T. Tsuruta, Bull. Soc. Chim. Jpn. 63 (1990) 3036;
(c) K. Kamahori, K. Ito, S. Itsuno, J. Org. Chem. 61 (1996) 8321;
(d) B. Mirviss, J. Org. Chem. 54 (1989) 1948.
[15] (a) H. Stöver, P. Lu, M. Fréchet, Polym. Bull. 25 (1991) 575;
(b) A. Hirao, M. Hayashi, S. Nakahama, Macromolecules 29 (1996) 3363.
[16] J. Kochi, Organometallic Mechanisms and Catalysis (Chapter 14), Academic Press, New York, 1978.
[17] M. Kobayashi, M. Kobayashi, Bull. Chem. Soc. Jpn. 59 (1986) 2807.
[18] M. Kobayashi, M. Yoshida, M. Kobayashi, Bull. Chem. Soc. Jpn. 59 (1986) 3169.
[19] (a) W. Reynolds, G. Hammer, A. Bassindale, J. Chem. Soc. Perkin Trans. II (1977) 971;
(b) Y. Nagasaki, K. Kurosawa, T. Tsuruta, Bull. Chem. Soc. Jpn. 63 (1990) 3036.
[20] T. Tursunbaev, Z. Manulkin, Zh. Obshch. Khim. 37 (1967) 219.
[21] T. Nakano, M. Kosugi, T. Migita, Main Group Chem. 1 (1996) 287.
[22] (a) P. Mazerolles, Bull. Soc. Chim. Fr. (1960) 856;
(b) J.-C. Masson, M. LeQuan, P. Cadiot, Bull. Soc. Chim. Fr. 3 (1967) 777.
[23] K. Mochida, N. Matsunhige, J. Organomet. Chem. 229 (1982) 11.
[24] (a) J.A. Soderquist, J. Organomet. Chem. 156 (1978) 227;
(b) E. Lukevics, P. Arsenyan, S. Belyakov, J. Popelis, Main Group Met. Chem. 21 (1998) 557;
(c) J.A. Soderquist, A. Negron, J. Org. Chem. 54 (1989) 2462.
[25] (a) M. Castany, H. Lavayssiere, G. Dousse, Synth. React. Inorg. Met.-Org. Chem. 28 (1998) 781;
(b) P. Mazerolles, F. Grégoire, R. Morancho, A. Reynes, N. Sefiani, J. Organomet. Chem. 328 (1987) 49.
[26] (a) D. Kolesnikow, Zh. Obshch. Khim. 29 (1959) 2042;
(b) E. Chernyshev, I. Zhukova, T. Krasnova, L. Freidin, Zh. Obshch. Khim. 38 (1968) 504.
[27] (a) N. Yamazaki, S. Nakahama, A. Hirao, Y. Shiraishi, H. Phung, Contemp. Top. Polym. Sci. 4 (1984) 379;
(b) A. Hirao, Y. Shiraishi, F. Martinez, H. Phung, S. Nakahama, N. Yamazaki, Makromol. Chem. 184 (1984) 961.
[28] K. Mizuno, K. Nakanishi, T. Toshisugu, Y. Sawada, Y. Otsuji, Chem. Lett. 8 (1993) 1349.