Pergamon

Tetrahedron Letters 44 (2003) 1647–1649

TETRAHEDRON LETTERS

Synthesis of *para*-substituted styrenes

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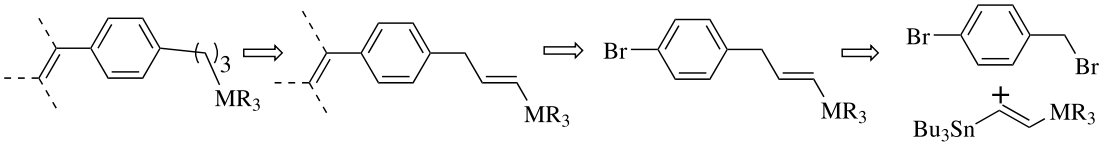
Received 19 November 2002; revised 20 December 2002; accepted 20 December 2002

Abstract—Using double Stille cross-coupling reaction bromo (or chloro)benzylbromide is easily transformed into substituted styrene monomers bearing a wide range of substituents in *para* position

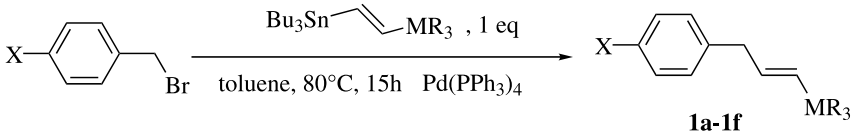
In continuation of our work on the synthesis of organic materials (Inertial Confinement Fusion program)[1] in the form of co-polymer polystyrene-modified-polystyrene in which the modified polystyrene is made from styrene monomers substituted in the *para* position by a spacer bearing an atom of the 14 group (Si, Ge or Sn), this type of monomer was required for polymerisation in order to test the physical properties of the co-polymers obtained. We have already described the synthesis of such styrene monomers with an $n=0$ or 1 carbon spacer between the aromatic group and an atom of the 14 group under ultrasound conditions.[2] A possible method to introduce a three carbon spacer ($n=3$) between the phenyl group and the trialkyl(or triphenyl)metal group is shown in the retrosynthetic scheme below (Scheme 1).

As can be seen in Scheme 1, vinyltin reagents are good candidates for such synthesis and have proved to be efficient tools for the transfer of a vinyl unit, with high tolerance of numerous functions both on the substrate and on the reagent.[3] The other reagent needed as starting material for such a synthesis is *p*-bromo-(chloro)benzyl bromide which is inexpensive.

In view of the surprising lack of literature reports on the reactivity of the two bromine atoms of *p*-bromobenzyl bromide and recognizing that a chemoselective reaction could be useful, we decided to take a close look at the substitution reaction under Stille cross-coupling reaction[4] in the presence of palladium complex catalysis.[5] We started from vinyltin compounds bearing a trialkylsilyl, trialkyl (or triphenyl)germyl or a tributyl-



Scheme 1.



Scheme 2.

Keywords: styrenes; palladium catalyst; coupling reactions.

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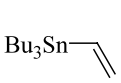
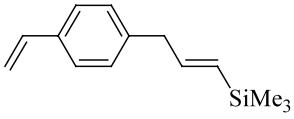
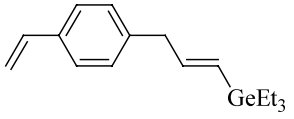
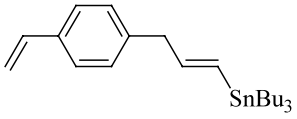
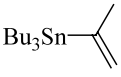
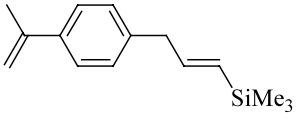
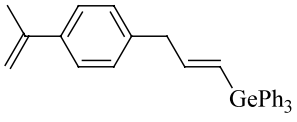
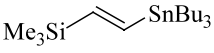
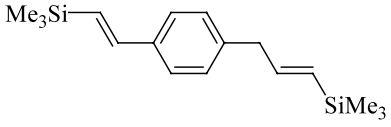
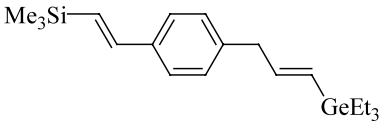
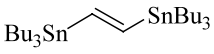
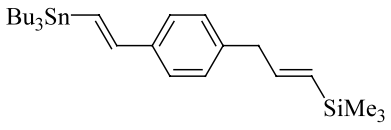
0040-4039/03/$ - see front matter
PII: S0040-4039(03)00027-3

Table 1.

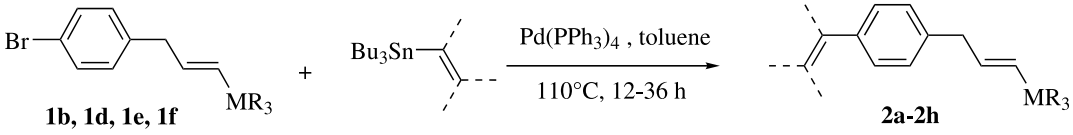
Entry	MR_3	X	Yield (%)	No
1	$SiMe_3$	Cl	68	**1a**
2	$SiMe_3$	Br	78	**1b**
3	$GeEt_3$	Cl	76	**1c**
4	$GeEt_3$	Br	80	**1d**
5	$GePh_3$	Br	67	**1e**
6	$SnBu_3$	Br	25	**1f**

stannyl group at the β-position. These compounds are obtained by hydrostannation of the corresponding alkynes under the experimental conditions used for the synthesis of (*E*)-1,2-bis(tributylstannyl)ethylene.[6] We are able to selectively substitute only the bromine atom in the benzylic position if we use 1 equiv. of the starting vinyltin, toluene as solvent and 3% mol of tetrakis(triphenylphosphine) palladium(0) as catalyst (Scheme 2, Table 1). Only the MR_3 group is transferred and no competition occurs with the possible transfer of the vinylstannyl unit (entries 1–5).[6c,7]

Table 2.

Entry	MR_3	Vinyltin	Product	Yield[a] %	N°
1	$SiMe_3$			75	**2a**
2	$GeEt_3$	"		71	**2b**
3	$SnBu_3$	"		68	**2c**
4	$SiMe_3$			69	**2d**
5	$GePh_3$	"		60	**2e**
6	$SiMe_3$			72	**2f**
7	$GeEt_3$	"		64	**2g**
8	$SiMe_3$			52	**2h**

[a]: isolated yield



Scheme 3.

As seen in the results reported in Table 1, we neither obtain bis-coupling products,[8] nor allylic compounds resulting from the conjugation of the external double bond with the aromatic ring, when the concentration of the solution is around 0.5 M. We also observe retention of the configuration of the double bond.

Another clean second substitution is also possible under Stille cross-coupling reaction providing as required acceptable yields of the new styrene monomers **2a**–**h** with an $n=3$ spacer between the aromatic group and the metal (Scheme 3).[9] The results are presented in Table 2.

In conclusion we report, through a double cross-coupling reaction, the synthesis of styrenes substituted in the *para* position by a wide range of substituents, with good overall yields, from commercially available bromobenzyl bromide. Some of the new compounds are currently tested for copolymerisation with styrene and provide promising results in terms of molecular weight, low polydispersity and physical properties (mechanical, thermal and solubility).

Acknowledgements

We thank the CNRS and MRT for providing financial support, and the 'Service d'analyse chimique du Vivant de Tours' for recording NMR and mass spectra.

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7. **Representative general procedure**: 0.04 g (3% mol) of tetrakis(triphenylphosphine)palladium(0) was added to a toluene solution (15 mL) of organic halide (1.15 mmol) after stirring for 15 min, 1.25 mmol of (*E*)-1-tributylstannyl-2-trialkyl (or triphenenyl)germylethylene diluted in 10 mL of toluene were added dropwise. The mixture was stirred overnight at 80°C. After cooling, the reaction mixture was filtered through a Celite path, and toluene was evaporated under reduced pressure. The residue was then treated with a 1 M solution of potassium fluoride and ethylacetate to eliminate the tributyltin halide thus formed. The aqueous layer was extracted with diethyl ether. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvents, the crude product was purified by column chromatography on silica gel (petroleum ether/triethylamine: 98/2). **1b**: ^{1}H NMR δ ppm ($CDCl_3$, 200 MHz): 0.12 (s, 9H), 3.45 (dd, $J=6.1$ Hz, $J=1.5$ Hz, 2H), 5.75 (dt, $J=18.4$ Hz, $J=1.5$ Hz, 1H), 6.17 (dt, $J=18.4$ Hz, $J=6.1$ Hz, 1H), 7.10 (m, 2H), 7.47 (m, $2H_{ar}$, m); ^{13}C NMR δ ppm ($CDCl_3$, 50 MHz): −1.2 (3C), 42.5, 119.8, 130.5, 131.4, 132.0, 138.8, 144.4; MS (70 eV) m/z: 255 ($M^{+\bullet}$−15, 26), 253 ($M^{+\bullet}$−15, 26), 159 (12), 137 (10), 116 (31), 115 (18), 90 (13), 89 (12), 74 (10), 73 (100), 59 (67), 58 (14), 45 (25), 43 (28). **1d**: ^{1}H NMR δ ppm ($CDCl_3$, 200 MHz): 0.86 (q, $J=6.4$ Hz, 6H), 1.06 (t, $J=7.2$ Hz, 9H), 3.46 (d, $J=5.8$ Hz, 2H), 5.82 (d, $J=18.2$ Hz, 1H), 6.06 (dt, $J=18.2$ Hz, $J=5.8$ Hz, 1H), 7.10 (d, $J=8$ Hz, 2H), 7.45 (d, $J=8$ Hz, 2H); ^{13}C NMR δ ppm ($CDCl_3$, 50 MHz): 4.7 (3C), 9.3 (3C), 43.0, 120.1, 129.0, 129.6, 130.8 (2C), 131.8 (2C), 139.6, 144.1; MS (70 eV) m/z: 358 ($M^{+\bullet}$−, 15), 356 ($M^{+\bullet}$−, 13), 211 (27), 209 (30), 102 (100), 91 (16).
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9. The compounds **2a**–**h** were obtained by the same methodology described in Ref. 7. **2a**: ^{1}H NMR δ ppm ($CDCl_3$, 200 MHz): 0.20 (s, 9H), 3.50 (dd, $J=6.3$ Hz, $J=1.4$ Hz, 2H), 5.27 (dd, $J=10.9$ Hz, $J=1.0$ Hz, 1H), 5.77 (dt, $J=18.4$ Hz, $J=1.4$ Hz, 1H), 5.79 (dd, $J=17.6$ Hz, $J=1.0$ Hz, 1H), 6.21 (dt, $J=18.4$ Hz, $J=6.3$ Hz, 1H), 6.77 (dd, $J=17.6$ Hz, $J=10.9$ Hz, 1H), 7.20 (d, $J=8.1$ Hz, 2H), 7.42 (d, $J=8.1$ Hz, 2H); ^{13}C NMR δ ppm ($CDCl_3$, 50 MHz): −1.2 (3C), 42.9, 113.0, 126.2 (2C), 128.9 (2C), 131.5, 135.4, 136.6, 139.7, 144.9; MS (70 eV) m/z: 216 ($M^{+\bullet}$, 21), 201 (16), 173 (11), 115 (13), 73 (100), 59 (46), 45 (18), 43 (14). **2b**: ^{1}H NMR δ ppm ($CDCl_3$, 200 MHz): 0.84 (q, $J=7.5$ Hz, 6H), 1.09 (t, $J=7.5$ Hz, 9H), 3.52 (d, $J=6.0$ Hz, 2H), 5.26 (dd, $J=10.8$ Hz, $J=0.8$ Hz, 1H), 5.77 (dd, $J=17.6$ Hz, $J=0.9$ Hz, 1H), 5.86 (dd, $J=18.2$ Hz, $J=0.9$ Hz, 1H), 6.12 (dt, $J=18.3$ Hz, $J=6.1$ Hz, 1H), 6.77 (dd, $J=17.6$ Hz, $J=10.9$ Hz, 1H), 7.21 (d, $J=8.1$ Hz, 2H), 7.41 (d, $J=8.1$ Hz, 2H); ^{13}C NMR δ ppm ($CDCl_3$, 50 MHz): 4.8 (3C), 9.4 (3C), 43.5, 113.5, 126.7 (2C), 129.0, 129.3 (2C), 135.8, 137.1, 140.5, 144.7; MS (70 eV) m/z: 304 ($M^{+\bullet}$, 8), 275 (100), 247 (38), 219 (21), 191 (20), 143 (13), 141 (17), 133 (16), 129 (20), 128 (35), 117 (21), 115 (37), 103 (34), 91 (20), 77 (11), 75 (12).